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Vibronic coupling in excited states of acetone

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Photoelectron spectroscopy of Rydberg states of acetone- h_6 and $-d_6$ populated by two- or three-photon excitation has been employed to unravel the vibronic description of excited-state levels. For the $3p$ Rydberg states vibronic transitions have been reanalyzed, leading to various reassignments and the observation of hitherto nonreported transitions. In addition, several ionic vibrational frequencies could be determined. At higher excitation energies previously identified, and in the present study newly identified, members of two Rydberg series have been characterized. The ns Rydberg series was explored up to the $8s$ state, the nd series up to the $7d$ state. Based upon the unambiguous assignments of vibronic character that we obtain for excited-state levels, various valence-Rydberg and Rydberg-Rydberg vibronic coupling pathways come to light and are analyzed.

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I. INTRODUCTION

Acetone is the simplest aliphatic derivative of the carbonyl family. As such, it is an obvious choice for studying the spectroscopic and dynamic properties of the excited states of this family of homologues. The photoresponse of carbonyl containing compounds, for example in the form of photodissociation of ketones, is important in photobiology for various reasons, amongst which the fact that three out of four DNA bases contain such functional groups. Because of its simplicity, small size, and central position in many areas of chemistry, the interpretation of the electronic spectrum of acetone has been, and still is subject of many spectroscopic studies. Theoretical studies of the spectroscopic properties of carbonyl compounds have, however, mainly been focused on formaldehyde (H_2CO).¹⁻³ A few *ab initio* studies on the excited states of acetone have been performed at various levels of sophistication.⁴⁻⁸ These calculations considered mainly the $n\pi^*$, $\pi\pi^*$, and $\sigma\pi^*$ valence states, as well as the lower-lying $n=3$ and $n=4$ Rydberg states

Acetone belongs to the C_{2v} symmetry point group, with the z -axis along the $C=O$ bond and the $CCOC$ skeleton in the yz plane and the electronic configuration $\dots(2b_1)^2(5b_2)^2(3b_1)^0$ in its 1^1A_1 ground state. Vibrational frequencies of the ground state have been compiled by Shimanouchi⁹ and are given in Tables I and II for acetone- h_6 and $-d_6$, respectively. For the comparison with other studies, particularly those of Goodman *et al.*¹⁰ and McDiarmid *et al.*,¹¹ it is important to notice that two notations seem to be in use. This alternative numbering of vibrations is indicated in the tables as well. The $\nu_{12}(a_2)$ antigeared and $\nu_{24}(b_1)$ (alternatively labeled as ν_{17}) gearing modes have attracted particular attention in the context of understanding torsional potential interactions in coupled methyl tops in the electronic ground, excited, and ionic states of acetone.^{10,12-15}

The highest occupied molecular orbital ($5b_2$) is a non-

bonding orbital, which in first approximation can be represented by the $2p_y$ atomic orbital on oxygen.⁷ Concentrating on the singlet manifold, we see that excitation from this lone pair orbital n_y to the $3b_1(\pi^*)$ orbital leads to the first excited singlet valence state 1^1A_2 that has its 0-0 transition at $30\,439.9145\text{ cm}^{-1}$.¹⁶ This dipole-forbidden transition has been the subject of many experimental studies¹⁷⁻²⁰ concentrating on aspects such as the role of vibronic coupling and interaction with triplet states.^{16,21,22} The first Rydberg state derives from excitation of a lone pair electron to the $3s$ Rydberg orbital, giving rise to the 1^1B_2 state located at 6.35 eV .^{14,23-26} Vibronic coupling comes prominently forward in the excitation spectra of this state by the activity of the $\nu_{12}(a_2)$ and $\nu_{24}(b_1)$ nontotally-symmetric vibrations.¹⁴

In the present study we will primarily be concerned with the $3p$ and higher Rydberg states. In particular the $3p$ Rydberg states have been the subject of extensive research, starting with various efforts to establish the order of the $3p_x$ (2^1A_2), $3p_y$ (2^1A_1), and $3p_z$ (2^1B_2) states.^{24,27} The comparison of the one-photon absorption spectrum with the two-photon resonance enhanced multiphoton ionization (REMPI) spectrum under linearly and circularly polarized excitation light conditions ultimately enabled the unambiguous assignment of the origin transitions found at 7.36 , 7.41 , and 7.45 eV as deriving from the $3p_x$, $3p_y$, and $3p_z$ states, respectively.^{11,24,27,28} Photoacoustic spectroscopy²⁸ demonstrated dramatic differences in the radiationless decay channels available to the three Rydberg states. In particular the $3p_y$ Rydberg state was considered to be subject to considerable mixing with the $\pi\pi^*$ (1^1A_1) valence excited state,²⁹ although for the $3p_z$ Rydberg state some mixing with an $n\sigma^*$ valence excited state was invoked as well.²⁸ Subsequent extensive studies of the two- and three-photon excitation spectra of the $3p$ Rydberg states and their polarization dependence led to assignments of active vibrations in the excitation spectrum.^{7,11,27} In these excitation spectra anoma-

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TABLE I. Experimental and *ab initio* vibrational frequencies (cm^{-1}) of ground, excited, and ionic states of acetone- h_6 .^a

(Sym.)	ν	Mode	Alt. ^b	X^1A_1	$3p_x(^1A_2)$	$3p_y(^1A_1)$	$3p_z(^1B_2)$	$X^2B_2^c$	B3LYP $X^2B_2^d$
a_1	1	CH ₃ -d-stretch		3019		3128	3148		3084
a_1	2	CH ₃ -s-stretch		2937		2424			2940
a_1	3	CO stretch		1731	1468 ^e			1541 ^e (1548)	1570
a_1	4	CH ₃ -d-deform		1435	1395 ^e		1376 ^e	1410 ^e	1395
a_1	5	CH ₃ -s-deform		1364	1293	1309	1280 ^e	(1288)	1269
a_1	6	CH ₃ rock		1066	1050 ^e	1058 ^e	1042 ^e	1046 ^e (1049)	1045
a_1	7	CC stretch		777				682 ^e	675
a_1	8	CCC deform		385 ^f	326.2	324 ^e	316 ^e	339 ^e (313)	321
a_2	9	CH ₃ -d-stretch		2963					3007
a_2	10	CH ₃ -d-deform		1426	1432 ^e			1484 ^e	1400
a_2	11	CH ₃ rock		877	892 ^e				868
a_2	12	Torsion		77.8	70.8	70		66.7	-49
b_2	13	CH ₃ -d-stretch	18	3019					3083
b_2	14	CH ₃ -d-stretch	19	2937					2933
b_2	15	CH ₃ -d-deform	20	1410					1385
b_2	16	CH ₃ -s-deform	21	1364					1313
b_2	17	CC stretch	22	1216					984
b_2	18	CH ₃ -rock	23	891			868 ^e		882
b_2	19	CO ip-bend	24	530			366 ^e	359 ^e	350
b_1	20	CH ₃ -d-stretch	13	2972					3014
b_1	21	CH ₃ -d-deform	14	1454					1424
b_1	22	CH ₃ -rock	15	1091					1032
b_1	23	CO op-bend	16	484 ^f	453	484			454
b_1	24	Torsion	17	124.5	129.4				116

^aExperimental frequencies taken from Refs. 9, 11, 13, 15, 25, except those labeled e.

^bAlternative numbering employed for example in Refs. 11 and 13.

^cFrequencies reported in the He(I) photoelectron study of Ref. 41 are given in parentheses.

^dAfter scaling with factor 0.9614 (Ref. 48).

^eFrequency determined in present work.

^fAssignments of ν_8 and ν_{23} in the ground state have been subject of discussion (Refs. 9, 16, 27, 49).

lously intense vibrational bands at high vibrational energies could be observed that were attributed to the effects of vibronic coupling with the $\pi\pi^*$ state. Their presence led to an approximate location of the $\pi\pi^*$ state between 7.5 and 7.7 eV, approximately where the $\pi\pi^*$ and A_1 $3p_y$ Rydberg potential curves were calculated to cross. Despite many efforts, however, direct observation of this valence excited state has been unsuccessful.

Starting with the $3d$ Rydberg states, information on the higher excited states becomes scarcer. Partly on the basis of *ab initio* calculations, the $3d_{x^2-y^2}$ (3^1B_2) and $3d_{xy}$ (2^1B_1) Rydberg states were assigned to three-photon resonances found at 8.09 and 8.17 eV, while the $3d_{yz}$ (3^1A_1) state was associated with a diffuse broad absorption band around 7.8 eV.⁷ This state was proposed to be perturbed by the $\pi\pi^*$ valence state in a similar way as the $3p_y$ Rydberg state. In the same multiphoton ionization study, two of the three $4p$ Rydberg states were identified at 8.55 and 8.60 eV on the basis of their quantum defect. Evidence for Rydberg states higher than $4p$ has been reported in two early absorption studies.^{30,31} At that time, however, no conclusive assignments were made.

In the present work we will apply excited-state photoelectron spectroscopy to study the spectroscopic and dynamic properties of the Rydberg manifold of acetone starting with the $3p$ Rydberg states. As amply demonstrated in previous studies,³²⁻³⁶ this approach has unique advantages over the commonly employed approach of mass-resolved ion de-

tection, since in general it allows the unambiguous identification of the (ro)vibronic character of the excited state from which ionization took place. Put in another way, one might say that the projection of the wave function of the excited state on the ionic manifold, as done in the photoionization step, ultimately enables the reconstruction of this wave function. As will be shown, these characteristics enable us to elucidate various aspects of the electronic structure of acetone, in particular those related to vibronic coupling between excited states. Although previous studies have paved the way for the assignment of the rich vibrational structure observed in the excitation spectra of the $3p$ Rydberg states,^{7,11} the fact that these three states are energetically so close together has inhibited a definite assignment of all resonances. Indeed, it will become clear that various previous assignments need to be revised or refined. At higher excitation energies previously identified Rydberg states have been characterized, and new states identified up to the $8s$ Rydberg state. A common theme evident from all photoelectron spectra is that vibronic coupling pervades at all possible levels, be it between Rydberg and valence states, be it between the various components of one Rydberg state, e.g., $3p_x$, $3p_y$, and $3p_z$, or be it between Rydberg states with Rydberg electrons of different angular momentum or principal quantum number. In fact, it will be shown that in the present study some of the identified Rydberg states are "unobservable" in our excitation spectra, but become observable by vibronic coupling in the photoelectron spectra of other states. Finally,

TABLE II. Experimental and *ab initio* vibrational frequencies (cm^{-1}) of ground, excited, and ionic states of acetone- d_6 .^a

(Sym.)	ν	Mode	Alt. ^b	X^1A_1	$3p_x(^1A_2)$	$3p_y(^1A_1)$	$3p_z(^1B_2)$	X^2B_2	B3LYP $X^2B_2^c$
a_1	1	CH ₃ -d-stretch		2264	2433		2411		2291
a_1	2	CH ₃ -s-stretch		2123	2165	1792			2108
a_1	3	CO stretch		1732					1534
a_1	4	CH ₃ -d-deform		1080	1028 ^d		1022 ^d	1030 ^d	1023
a_1	5	CH ₃ -d-deform		1035	969 ^d			966 ^d	967
a_1	6	CH ₃ rock		887	823 ^d	832 ^d	817 ^d	798 ^d	826
a_1	7	CC stretch		689	672	660	665	669 ^d	633
a_1	8	CCC deform		320 ^e	279.5	278 ^d	275 ^d	234 ^d	277
a_2	9	CH ₃ -d-stretch		2205					2228
a_2	10	CH ₃ -d-deform		1021	1109 ^d			1113 ^d	1012
a_2	11	CH ₃ rock		669	671 ^d			678 ^d	657
a_2	12	Torsion		53.4	49.1			42.4	-34
b_2	13	CH ₃ -d-stretch	18	2264					2287
b_2	14	CH ₃ -s-stretch	19	2123					2103
b_2	15	CH ₃ -d-deform	20	1004			877 ^d		898
b_2	16	CH ₃ -s-deform	21	1035					988
b_2	17	CC stretch	22	1242					1033
b_2	18	CH ₃ -rock	23	724					704
b_2	19	CO ip-bend	24	475			345 ^d	355 ^d	332
b_1	20	CH ₃ -d-stretch	13	2227					2232
b_1	21	CH ₃ -d-deform	14	1050					1025
b_1	22	CH ₃ -rock	15	960					888
b_1	23	CO op-bend	16	405 ^e					383
b_1	24	Torsion	17	96.0	98.2	100			87

^aExperimental frequencies taken from Refs. 9, 11, 13, 15, 25, except those labeled d.

^bAlternative numbering employed for example in Refs. 11 and 13.

^cAfter scaling with factor 0.9614 (Ref. 48).

^dFrequency determined in present work.

^eAssignments of ν_8 and ν_{23} in the ground state have been subject of discussion (Refs. 9, 16, 27, 49).

as a spin-off, the present study has enabled the determination of the, until now, unknown frequency of several vibrations in the ground state of the acetone radical cation.

II. EXPERIMENTAL AND THEORETICAL DETAILS

The setups we use have been described in great detail previously^{37,38} and will therefore only be summarized briefly here. In our experiments we partly made use of samples seeded into supersonic expansions, but also performed studies using effusive beams. The high-resolution (2+1) resonantly enhanced multiphoton ionization (REMPI) spectra and photoelectron spectra (PES) of supersonically cooled acetone and deuterioacetone have been measured using a pulsed dye laser running on DCM dissolved in DMSO (Lumonics Hyperdye-300), which was pumped by a XeCl excimer laser (Lambda Physik EMG103MSC). This excimer laser gives 10 ns pulses with a maximum pulse energy of 200 mJ and is typically used at a repetition rate of 30 Hz. The dye laser output was frequency doubled using an angle-tuned KD*P crystal in an INRAD II autotracker and focused by a 25 mm quartz lens into the ionization region of the spectrometer. This spectrometer consists of a 2π analyzer that has been slightly modified from the original design by Kruit and Read,³⁹ and has been interfaced with a pulsed molecular beam. In the ionization region of the spectrometer a strongly diverging magnetic field parallelizes the trajectories of the electrons produced in a laser shot. The kinetic energies of the electrons are subsequently analyzed by means of a time-of-

flight technique. After detection by a pair of microchannel plates, the signal is stored in a 500 MHz digital oscilloscope (Tektronix TDS540), which is connected to a computer (Intel 80486 DX2 66 MHz).

An excitation spectrum is constructed by integration of (part of) the photoelectrons over the scanned wavelength region. Photoelectron spectra are recorded by increasing in steps the retarding voltage on a grid surrounding the flight tube, and transforming each time only the high-resolution part of the time-of-flight spectrum. In this way, an optimum energy resolution of about 10 meV can be obtained for all kinetic energies. The energy scale of the photoelectrons as well as the laser wavelengths were calibrated using multiphoton resonances of krypton or xenon.⁴⁰

The pulsed supersonic expansion is generated by expansion of 3 bar He mixed with room-temperature acetone vapor through a 0.5 mm diam pulsed nozzle (General Valve Iota One System) into a chamber that is pumped by an Edwards Diffstak 2000 oil diffusion pump backed by an Edwards E2M40 rotary pump. The expansion chamber is connected through a Beam Dynamics skimmer with a diameter of 0.5 mm to the ionization chamber, which in turn is evacuated by a Balzers TPH 170 turbomolecular pump backed by a Leybold Trivac D16B rotary pump. The flight tube is pumped by a Leybold Turbovac 450 turbomolecular pump backed by a Leybold Trivac D16B rotary pump. A pulse duration of typically 200 μs at a repetition rate of 30 Hz resulted in a pressure in the expansion chamber of about 6×10^{-5} mbar. With-

out gas input the pressure is about 1×10^{-7} mbar. The pressure in the flight tube is typically 1×10^{-7} mbar, and remains basically the same under operating conditions. A homebuilt delay generator is used to control the timing of the gas pulse relative to the laser pulse.

(3 + 1) REMPI experiments have been performed on effusively introduced samples using a laser system that consists of a pulsed dye laser (Lumonics Hyperdye-500, bandwidth $\sim 0.08 \text{ cm}^{-1}$) pumped by a Lumonics HyperEx-460 excimer laser. For the (3 + 1) experiments several dyes have been used: Coumarine 480, 460, and 440 and Exalite 428, 416, 411, 404, 398, and 389. The laser beam is in these effusive experiments focused into the ionization region of a first-generation magnetic bottle electron spectrometer by a 25 mm quartz lens. Commercially available acetone- h_6 and - d_6 were used as supplied.

In conventional electron-detected excitation spectroscopy all photoelectrons, irrespective of their kinetic energies, are collected and their yield monitored during the scan. In the present study we will be interested in monitoring electrons that derive from ionization to very well-defined ionic levels. In order to accomplish this with a good energy resolution, we have to retard the electrons in the flight tube, but at the same time take care that during a scan over a rather large energy range these electrons still arrive within a preset gate. This has been realized by employing a wavelength-dependent retarding voltage on the flight tube.

For the analysis of our high-resolution photoelectron spectra it turned out to be necessary to have a rather accurate idea of ionic vibrational frequencies. In the past a few of these frequencies have been determined,^{10,15,41} but not enough to serve our purpose. Following previously reported calculations,¹⁰ we have therefore performed *ab initio* calculations of the equilibrium geometry and the associated harmonic force field at the UB3LYP/6-31G* (Refs. 42–44) level employing the GAUSSIAN suite of programs.⁴⁵ These calculations have been done assuming C_{2v} symmetry of the molecule with an eclipsed–eclipsed geometry of the methyl groups, and lead to the frequencies reported in Tables I and II for acetone- h_6 and - d_6 , respectively. From these tables it can be seen that for ν_{12} an imaginary frequency is calculated. We do not interpret this as an indication for a departure from C_{2v} symmetry in the X^2B_1 ionic ground state, rather that at this level the employed method is not adapted to deal with the flat potential energy surface along ν_{12} . Indeed, other studies¹⁰ report that the eclipsed–eclipsed geometry of the molecule is a stable minimum on the potential energy surface of the radical cation.

III. RESULTS AND DISCUSSION

A. (2 + 1) REMPI-PES of supersonically cooled acetone- h_6 and - d_6

In Fig. 1 the two-photon resonance enhanced multiphoton ionization spectra of supersonically cooled acetone- h_6 and acetone- d_6 in the two-photon energy range of 59 200–62 200 cm^{-1} are shown. In this excitation region the $3p$ Rydberg states have been located previously.^{10–13,15,24,27–29} The excitation spectra show various resonances that are tabu-

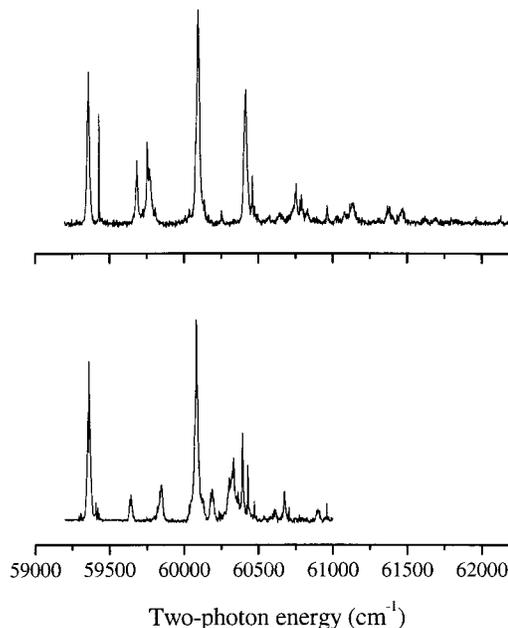


FIG. 1. (2 + 1) REMPI spectrum of jet-cooled acetone- h_6 (top) and acetone- d_6 (bottom).

lated in Tables III and IV for acetone- h_6 and - d_6 , respectively. Their assignments have been done on the basis of photoelectron spectra recorded at these resonances, utilizing the calculated ionic frequencies referred to in the previous section. The vibrational frequencies that have been determined for the various states on the basis of these assignments are collected in Tables I and II for acetone- h_6 and - d_6 , respectively. Although this particular part of the excitation region has been extensively investigated in the past,¹¹ it will become clear that the application of excited-state photoelectron spectroscopy leads to new insights in the spectroscopic and dynamic properties of the excited states. To this purpose we will show and discuss in the following some typical photoelectron spectra.

The (2 + 1) photoelectron spectrum of acetone- h_6 taken at the 0–0 transition to the $3p_x(^1A_2)$ state ($59\,360 \text{ cm}^{-1}$) (Ref. 11) is depicted in Fig. 2(a). The spectrum shows only one peak with an energy of $1.333 \pm 0.005 \text{ eV}$, which—employing a lowest ionization energy of 9.708 eV (Ref. 15)—can be assigned as deriving from an ionization process, starting from a vibrationless ground state, $\mathbf{v}''=0$, to the vibrationless ionic state, $\mathbf{v}^+=0$. We will abbreviate such a $\mathbf{v}^+=0 \leftarrow \mathbf{v}''=0$ ionization as the $0''-0^+$ peak in the rest of this paper. The corresponding photoelectron spectrum for acetone- d_6 (not shown) was taken at $59\,363 \text{ cm}^{-1}$ and displays, apart from the dominant peak associated with ionization to the $\mathbf{v}^+=0$, a small peak shifted by 121 meV (976 cm^{-1}) from the $0''-0^+$ peak, which can be assigned to ionization to the $\nu_5^+=1$ level on the basis of the calculated ionic frequencies. The observation of a predominant $\Delta \mathbf{v} = \mathbf{v}^+ - \mathbf{v}'' = 0$ behavior strongly suggests that the equilibrium geometry and potential energy surface of the $3p_x$ Rydberg state and of the ground ionic state are very similar, in agreement with the conclusions drawn from previous ZEKE-PFI studies.^{10,15}

The photoelectron spectrum depicted in Fig. 2(b) was

TABLE III. Observed two- and three-photon transitions for acetone- h_6 and their assignments. Assignments given in bold concern transitions that either have been reassigned or were not reported in previous studies.

Two-photon $\bar{\nu}$ (cm $^{-1}$)	Three-photon $\bar{\nu}$ (cm $^{-1}$)	$3p_x(^1A_2)$		$3p_y(^1A_1)$		$3p_z(^1B_2)$	
		$\Delta\bar{\nu}^a$ (cm $^{-1}$)	Assignment	$\Delta\bar{\nu}^a$ (cm $^{-1}$)	Assignment	$\Delta\bar{\nu}^a$ (cm $^{-1}$)	Assignment
59 360		0	0_0^0				
59 430		70	12_0^1				
59 684		324	8_0^1				
59 756		396	$8_0^1 12_0^1$				
59 770	59 797			0	0_0^0		
59 810		450	$23_0^1 / 8_0^1 24_0^1$				
60 094	60 110			324	8_0^1	0	0_0^0
60 252		892	11_0^1				
64 410	60 440	1050	6_0^1	640	8_0^2	316	8_0^1
60 460						366	19_0^1
60 476		1116	$6_0^1 12_0^1$				
60 755		1395	4_0^1				
60 780						686	$8_0^1 19_0^1$
60 792	60 786	1432	10_0^1				
60 828		1468	3_0^1				
60 962						868	18_0^1
61 136	61 107					1042	6_0^1
61 374						1280	5_0^1
61 470	61 470					1376	4_0^1
	62 241			2471	2_0^1		
	62 559			2789	$2_0^1 8_0^1$		

^a $\Delta\bar{\nu}$ given relative to the two-photon origin transitions.

recorded at a two-photon energy of 59 684 cm $^{-1}$. This resonance was previously assigned to the $(3p_x)8_0^1$ transition.¹¹ In that case $\Delta\mathbf{v}=0$ behavior would lead us to expect that ionization via this resonance should predominantly lead to ions in the $\nu_8^+=1$ level. The spectrum shows a small peak at 1.396 \pm 0.005 eV deriving from ionization to the vibrationless ion, and an intense peak shifted 41 meV from the $0''-0^+$ peak, which indeed arises from ionization to the

$\nu_8^+=1$ level. This spectrum thus not only confirms the previous assignment,¹¹ but also gives insight in the vibrational frequencies in the ionic ground state of acetone. From this spectrum and others, we can conclude that the ν_8 ionic vibrational frequency is 42 \pm 3 meV (339 \pm 24 cm $^{-1}$). The $(3p_x)8_0^1$ transition in acetone- d_6 is found at 59 642 cm $^{-1}$. Ionization via this state leads to a photoelectron spectrum similar to the one obtained for acetone- h_6 ; an intense $\Delta\mathbf{v}$

TABLE IV. Observed two- and three-photon transitions for acetone- d_6 and their assignments. Assignments given in bold concern transitions that either have been reassigned or were not reported in previous studies.

Two-photon $\bar{\nu}$ (cm $^{-1}$)	Three-photon $\bar{\nu}$ (cm $^{-1}$)	$3p_x(^1A_2)$		$3p_y(^1A_1)$		$3p_z(^1B_2)$	
		$\Delta\bar{\nu}^a$ (cm $^{-1}$)	Assignment	$\Delta\bar{\nu}^a$ (cm $^{-1}$)	Assignment	$\Delta\bar{\nu}^a$ (cm $^{-1}$)	Assignment
59 363	59 377	0	0_0^0				
59 408		45	12_0^1				
59 642		279	8_0^1				
59 846	59 835			0	0_0^0		
60 034		671	11_0^1				
60 083	60 094					0	0_0^0
60 124				278	8_0^1		
60 186		823	6_0^1				
60 332		969	5_0^1				
60 358	60 369					275	8_0^1
60 391		1028	4_0^1	545	8_0^2		
60 428						345	19_0^1
60 472		1109	10_0^1				
60 678				832	6_0^1		
60 706						626	$8_0^1 19_0^1$
60 900						817	6_0^1
60 960						877	15_0^1
	61 105					1022	4_0^1
	61 327	1964	5_0^2				
	61 597			1751	2_0^1		

^a $\Delta\bar{\nu}$ given relative to the two-photon origins.

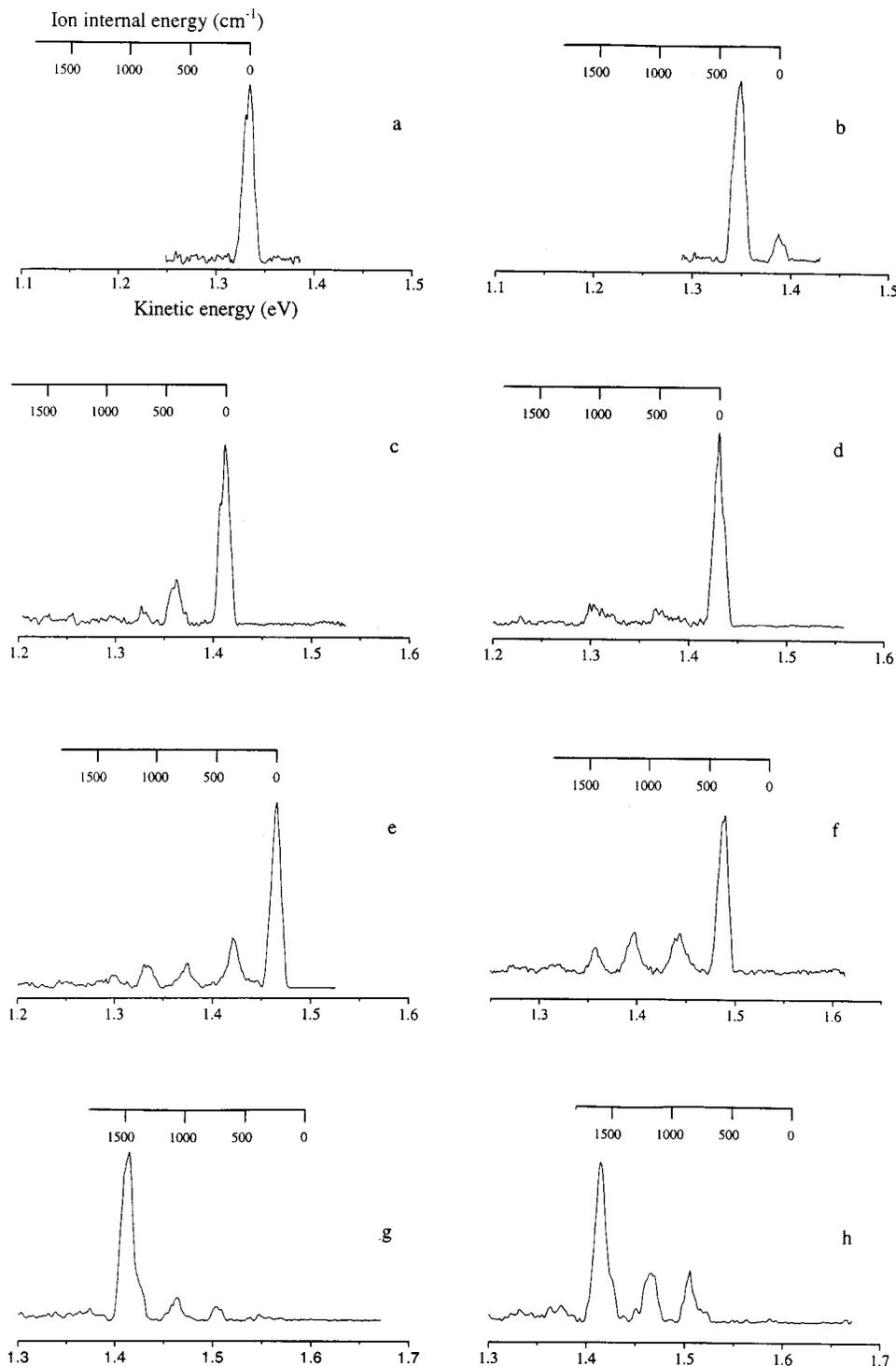


FIG. 2. (2+1) Photoelectron spectra of acetone- h_6 at (a) $59\,360\text{ cm}^{-1}$ [$(3p_x)0_0^0$]; (b) $59\,684\text{ cm}^{-1}$ [$(3p_x)8_0^1$]; (c) $59\,770\text{ cm}^{-1}$ [$(3p_y)0_0^0$]; (e) $60\,094\text{ cm}^{-1}$ [$(3p_z)0_0^0$ and $(3p_y)8_0^1$]; (f) $60\,460\text{ cm}^{-1}$ [$(3p_z)19_0^1$]; (g) $60\,792\text{ cm}^{-1}$ [$(3p_x)10_0^1$]; (h) $60\,828\text{ cm}^{-1}$ [$(3p_x)3_0^1$] and of acetone- d_6 at (d) $59\,846\text{ cm}^{-1}$ [$(3p_y)0_0^0$].

$=0$ peak is seen that is shifted by $29 \pm 5\text{ meV}$ ($234 \pm 40\text{ cm}^{-1}$) from a nonobservable $0''-0^+$ peak.

As yet, the photoelectron spectra exhibit rather expected behavior. This situation becomes quite different when ionization via the $0-0$ transition to the $3p_y(^1A_1)$ Rydberg state is considered. Normally, we would expect an intense $0''-0^+$ peak, and although the photoelectron spectrum shown in Fig. 2(c) does indeed show a $0''-0^+$ peak at $1.409 \pm 0.005\text{ eV}$, also two other peaks are seen. Under the supersonic conditions of our experiments our initial state is the vibration-less ground state. Within the Born-Oppenheimer

approximation⁴⁶ only excitation of totally-symmetric vibrational levels would be permitted, and ionization should thus in the end lead to ions that are also in totally-symmetric vibrational levels. The small peak displaced by 83 meV (669 cm^{-1}) from the $0''-0^+$ peak can indeed be assigned without problem to ionization to the $v_7^+(a_1)=1$ level (see Table I). However, the same table shows that an assignment of the peak shifted by 50 meV ($\sim 400\text{ cm}^{-1}$) in terms of a totally-symmetric vibrational level is not possible. We must therefore find another explanation for this peak. If we forget for the moment our symmetry considerations, we see that the

ionic $8^1 12^1$ vibrational level of a_2 symmetry would have the correct vibrational energy. Ionization to this level implies, however, excitation of the same vibrational level in the intermediate state. Now all pieces fall together because the only electronic state that would come into consideration to have this particular vibrational level close to the $3p_y$ state is the $3p_x(^1A_2)$ state. The vibronic symmetry of the $(3p_x)8^1 12^1$ level would then be A_1 , i.e., the same symmetry as the $3p_y$ Rydberg state. We thus have to come to the conclusion that the $(3p_x)8^1 12^1$ and $(3p_y)0^0$ levels are coupled on account of their near-degeneracy. As a result, the ionization process does not only reveal the $(3p_y)0^0$ character, but also the coupled $(3p_x)8^1 12^1$ character.

Excitation of the $(3p_y)0^0$ level in acetone- d_6 has been reported to occur at a significantly higher energy.²⁷ Ionization via this state was recorded at $59\,846\text{ cm}^{-1}$ and is shown in Fig. 2(d). We observe an intense peak at the $0''-0^+$ position at 1.430 eV. A small broad peak is observed shifted by 56 meV (452 cm^{-1}). Inspection of Table II leads once again to the conclusion that this energy cannot be assigned to a totally-symmetric ionic vibrational level. On the other hand, the value of 56 meV matches very well the energy difference between the origin transitions to the $3p_x$ and $3p_y$ states. If we therefore assume that the peak finds its origin in the coupling between a $3p_x$ vibrational level with a_2 symmetry and the $3p_y$ vibrationless level, we find that it corresponds either to ionization to the $8^1 12^3$ level (54 meV) or the $19^1 24^1$ level (52 meV). Notice that in the present case ionization to the $8^1 12^1$ level can definitely be ruled out—in that case a peak at 40 meV would have been expected. From the intensity of the various peaks in Fig. 2(d) it is clear that in acetone- d_6 the coupling of the $3p_y$ and the $3p_x$ states is less than in acetone- h_6 , in line with the observation that the energy gap between the two coupled levels is smaller in acetone- h_6 . The third peak, 122 meV (984 cm^{-1}) displaced from the $0''-0^+$ peak, is assigned to ionization to the 5^1 ionic level, as we observed previously for ionization via the vibrationless transition to the $3p_x$ state of acetone- d_6 .

In the last example a situation was encountered where we cannot unambiguously assign the ionic vibrational level to which ionization occurs, simply because there are various possibilities that cannot be discriminated with our experimental resolution. At the same time we know that the ionic vibrational energy matches well the energy difference between two excited states, which implies that we do know the electronic character of the coupled state. It is clear that the higher we will go in excitation energy, the more this will occur on account of the increase in vibrational level density.

The photoelectron spectrum recorded at the $3p_z(^1B_2)$ origin for acetone- h_6 is shown in Fig. 2(e). In line with our expectations an intense $0''-0^+$ peak is seen. We furthermore observe peaks shifted 43 meV (347 cm^{-1}), 92 meV (742 cm^{-1}), 131 meV (1057 cm^{-1}), and 169 meV (1363 cm^{-1}) from the $0''-0^+$ peak. Again we will try to assign these peaks to totally-symmetric vibrational levels. In this spirit, the peaks at 169 and 131 meV are readily assigned to $\nu_4^+ = 1$ and $\nu_6^+ = 1$, respectively. Since in acetone- h_6 the $(3p_y)8_0^1$ transition is almost degenerate with the $3p_z$ origin transition, one would most logically assign the peak at 43

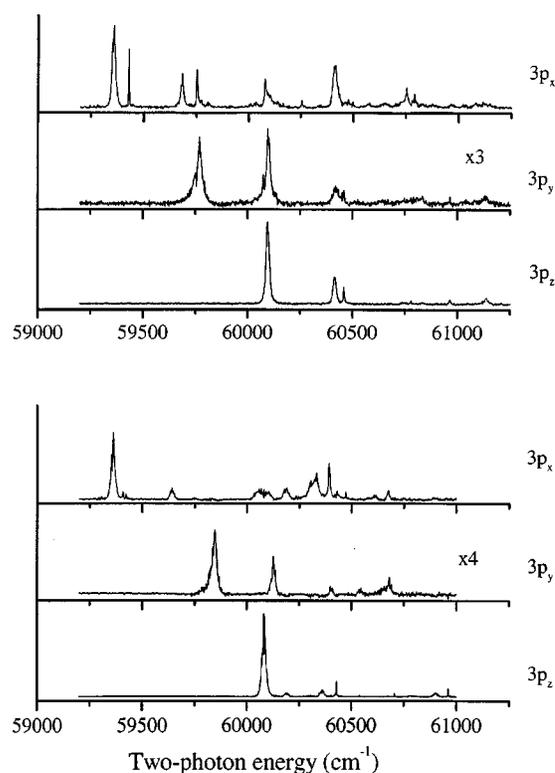


FIG. 3. (2+1) REMPI spectra of jet-cooled acetone- h_6 (top) and acetone- d_6 (bottom) separated into the contributions of $3p_x$, $3p_y$, and $3p_z$ Rydberg states.

meV to ionization to the $\nu_8^+ = 1$ level. This is, however, not the complete story. First, below we will show excitation spectra in which we can visualize the contributions of the individual Rydberg states to the various resonances (Fig. 3). The $3p_y$ trace shows there that the presumed $(3p_y)8_0^1$ transition has the same intensity as the $(3p_y)0_0^0$ transition. For the other two Rydberg states the 8_0^1 transition is significantly less intense than the 0_0^0 transition. Such a difference would *a priori* not be expected. Second, for acetone- d_6 the origin transition to the $3p_z$ state is not degenerate with the $(3p_y)8_0^1$ transition. The photoelectron spectrum obtained at the $(3p_z)0_0^0$ transition in acetone- d_6 shows, apart from an intense $0''-0^+$ peak, a peak at 40 meV (323 cm^{-1}) that cannot be assigned to a totally-symmetric level, but matches very well the ionic frequency of the CO in-plane-bend ν_{19} of b_2 symmetry. This vibration is predicted to have an ionic frequency of 350 cm^{-1} in acetone- h_6 (Table I), and it may thus well be that the 43 meV peak in the photoelectron spectrum of acetone- h_6 contains a contribution of ionization to the ionic 19^1 level as well, thereby giving an explanation for the intensity anomaly noticed above. From the activity of ν_{19} in the photoelectron spectra we can conclude that vibronic coupling occurs between the $3p_z(^1B_2)$ and $3p_y(^1A_1)$ states.

For the 92 meV (742 cm^{-1}) peak in Fig. 2(e) no appropriate a_1 vibrational level can be found. We notice that this energy is close to the energy difference between the $3p_x$ and $3p_z$ Rydberg states. It is therefore reasonable to assume that this peak results from the coupling of a $3p_x$ vibrational level with the $3p_z$ Rydberg state. Various possibilities such as the $8^1 23^1$ (96 meV), $7^1 24^1$ (98 meV), or even the $8^1 12^1 19^1$ (93

meV) come to mind. The observation of a peak at 89 meV (718 cm^{-1}) in the corresponding photoelectron spectrum of acetone- d_6 would slightly favor the $7^1 2_4^1$ assignment, but in the end there are simply too many possibilities that cannot be distinguished unambiguously with our experimental resolution. On top of that, it should be realized that because of different energy gaps, nontotally symmetric vibrational levels that are prominently visible for acetone- h_6 may not be visible for acetone- d_6 and vice versa. What can be said with reasonable certainty is, however, that the 92 meV (89 meV for $-d_6$) peak finds its origin in the ionization of a vibrational level of the $3p_x$ Rydberg state.

The above examples, and many others not discussed here, clearly show that the dominant peaks in the photoelectron spectra derive from $\Delta v=0$ ionization processes, be it from accessible vibrational levels of a certain Rydberg state, be it from levels that have become accessible by vibronic coupling. This implies that, when comparing ionization via two different resonances associated with one particular Rydberg state, the kinetic energy of photoelectrons can be expected to have an absolute energy shift that is equal to the shift in photon energy. By setting gates in the time-of-flight spectrum on photoelectron peaks associated with $\Delta v=0$ ionization from the $3p_x$, $3p_y$, and $3p_z$ Rydberg states, and compensating for changes in the electron kinetic energies when the excitation wavelength is scanned by adjusting the electric field in the flight tube—thus realizing that these photoelectrons always arrive at the same time at the detector—we are able to dissect the spectrum previously shown in Fig. 1 into the contributions of the $3p_x$, $3p_y$, and $3p_z$ Rydberg states. The results for both acetone- h_6 and acetone- d_6 are shown in Fig. 3. These spectra immediately show the previously discussed coupling between the three $3p$ states. An almost textbook example of the mixing of a bright and a dark state can be seen when the excitation spectrum of the 0–0 transition to the $3p_y$ state is considered (Fig. 4). When electrons deriving from ionization of $3p_x$ and $3p_y$ levels are monitored separately, a dip is observed in the $3p_y$ channel at $59\,756\text{ cm}^{-1}$. This dip is exactly at the same place as the $8^1 12^1$ level of the $3p_x$ state. Mixing of the two levels results in a redistribution of intensity and we consequently see intensity appearing in the $3p_x$ channel at the same time that the intensity decreases in the $3p_y$ channel.

Another aspect of interest of the excitation spectra that is now elucidated are the rotational contours of the various resonances, which are seen to occur either as sharp or relatively broad. For identical photons—as is the case for the single laser experiments we are reporting here—the two-photon $T_{\pm 2, \pm 1, 0}^2$ and the T_0^0 transition tensors may induce transition intensity.^{13,47} The former transition tensors give rise to $\Delta J=0, \pm 1$, and ± 2 rotational transitions, the latter only to $\Delta J=0$ transitions. Simulations employing rotational constants of the ground state of the neutral and radical cation confirm the suspicion that the sharp features should be interpreted as indicating a dominance of the T_0^0 tensor for these transitions. Because this tensor is totally-symmetric, we would in first instance expect the narrow resonances to be associated with transitions to the $3p_y(^1A_1)$ state. Such is not the case, as is clearly demonstrated in Fig. 3; transitions to

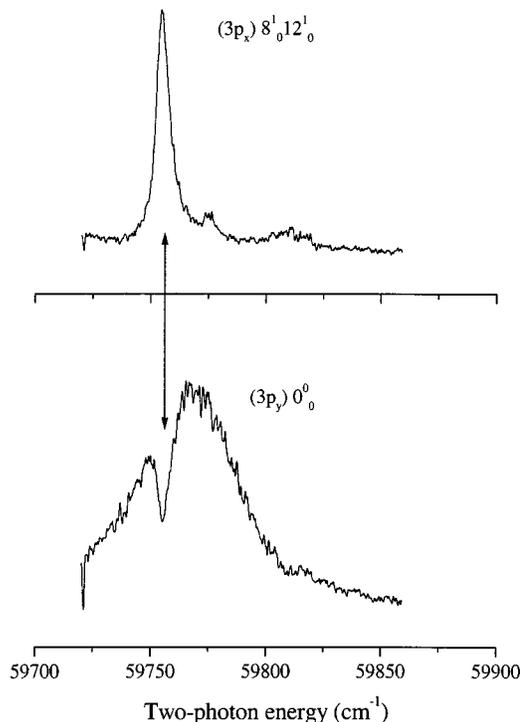


FIG. 4. Expanded view of the (2+1) REMPI spectrum of jet-cooled acetone- h_6 at the quasidegenerate $(3p_x)12_0^1 8_0^1$ and $(3p_y)0_0^0$ transitions.

the $3p_y$ levels appear as “broad” features, while the “sharp” features are all associated with vibronically induced transitions to the $3p_x$ and $3p_z$ states. The observation that transitions to $3p_y$ levels appear as broad features while they would be expected to be narrow indicates that they are lifetime broadened. This would be in line with previous suspicions that the $3p_y$ state is subject to vibronic coupling with the valence excited $\pi\pi^*(^1A_1)$ state. Photoacoustic measurements^{28,29} give ample reason to believe that this $\pi\pi^*$ state has a very short lifetime, and its mixing with the $3p_y$ state would thus lead to a shortening of the lifetime of this state—in agreement with our observations. Although our photoelectron spectra do not exhibit any direct signature of this $3p_y-\pi\pi^*$ vibronic coupling, we can conclude that the excitation spectra indirectly give evidence for its presence.

From the traces shown in Fig. 3, and the previously determined polarization behavior of the resonances¹¹ we are now able to come to the unambiguous assignments given above in Tables III and IV. Our assignments differ in a number of cases with those of previous studies. In Tables III and IV these assignments are indicated in bold. In the following a number of the more prominent differences will be discussed.

The sharp line in the $3p_x$ channel spectrum at $60\,252\text{ cm}^{-1}$, 892 cm^{-1} above the 0–0 transition, has been observed,¹¹ but was not assigned. Its small width indicates that we deal here with a vibrational level of a_2 symmetry, and thus with a transition that obtains transition intensity by coupling with the $3p_y$ state. The most likely candidate is the CH_3 rock vibration ν_{11} . The corresponding $3p_x$ channel in acetone- d_6 shows a small sharp line 671 cm^{-1} shifted from the 0–0 transition. Upon deuteration the frequency of ν_{11} is

observed to decrease from 877 to 669 cm^{-1} in the neutral ground state,⁹ and predicted to decrease from 868 cm^{-1} to 657 cm^{-1} in the ionic state. We can consequently safely assign the resonance to $(3p_x)11_0^1$ transition.

The resonance at 60 460 cm^{-1} in the excitation spectrum of acetone- h_6 was previously assigned to the $(3p_y)23_0^2$ transition.¹¹ Figure 3 shows that at this excitation energy activity is observed in both the $3p_y$ and the $3p_z$ channels. Because of (i) its position—366 cm^{-1} to the blue of the $3p_z$ origin—and (ii) its small width, we conclude that we deal here with the $(3p_z)19_0^1$ transition. Confirmation is found in the corresponding photoelectron spectrum [Fig. 2(f)] that does not show a $0''-0^+$ transition, but a peak shifted by 46 meV from the theoretical $0''-0^+$ peak. The spectrum in Fig. 2(f) shows a similar intensity pattern as seen in Fig. 2(e) for ionization via the $0-0$ transition to the $3p_z$ state, all peaks being displaced, however, by the energy of the 19^1 ionic level. The peaks displaced by 92 meV and 139 meV can now easily be assigned as deriving from ionization from levels associated with the $3p_y$ and $3p_x$ states, while the peaks shifted by 219 meV and 179 meV from the $0''-0^+$ peak correspond to ionization to the $4^1 19^1$ and $6^1 19^1$ ionic levels, respectively. No evidence is found for a $(3p_y)23_0^2$ transition.¹¹ In acetone- d_6 we observe a similar transition at 60 428 cm^{-1} that was previously assigned to the $(3p_y)23_0^2$ transition as well. On similar grounds as for acetone- h_6 we revise this assignment to the $(3p_z)19_0^1$ transition.

At 60 755 cm^{-1} a broad line is observed for acetone- h_6 for which a photoelectron spectrum is obtained that shows only one intense peak shifted by 179 meV (1443 cm^{-1}) from the $0''-0^+$ transition. This observation is at odds with the previous $(3p_y)8_0^3$ assignment, but would rather indicate ionization to the $\nu_4^+ = 1$ level. Since the 60 755 cm^{-1} resonance is shifted by 1395 cm^{-1} from the $(3p_x)0_0^0$ transition, we reassign it to the $(3p_x)4_0^1$ transition. The same transition is found for acetone- d_6 at 60 395 cm^{-1} , 1032 cm^{-1} displaced from the $(3p_x)0_0^0$ transition. The associated photoelectron spectrum shows an intense peak 124 meV (1000 cm^{-1}) from the $0''-0^+$ transition in agreement with the revised assignment.

The resonance observed at 60 792 cm^{-1} in acetone- h_6 was previously thought to derive from the $(3p_y)6_0^1$ transition.¹¹ Its width and presence in the $3p_x$ channel indicates, however, that we deal here with a vibronic level of A_1 symmetry. Because the resonance is displaced by 1432 cm^{-1} from the $3p_x$ origin transition, we assign it as the $(3p_x)10_0^1$ transition. The photoelectron spectrum depicted in Fig. 2(g) does not show a $0''-0^+$ transition, but an intense peak at 184 meV (1484 cm^{-1}) that supports our assignment. Small peaks shifted by 134 meV (1081 cm^{-1}) and 95 meV (766 cm^{-1}) correspond to ionization from levels associated with $3p_y$ and $3p_z$. In acetone- d_6 a similar resonance is observed in the $3p_x$ channel at 60 472 cm^{-1} . This resonance was assigned as the $(3p_y)7_0^1$ transition,¹¹ but since (i) the photoelectron spectrum reveals an intense peak 138 meV (1113 cm^{-1}) from the $0''-0^+$ transition, (ii) it is 1110 cm^{-1} shifted from the $(3p_x)0_0^0$ transition, and (iii) its width does not support a transition to a $3p_y$ vibrational level, we conclude that we deal here with the $(3p_x)10_0^1$ transition.

We finally consider the resonance observed at 60 828 cm^{-1} in the $3p_x$ channel of acetone- h_6 , previously assigned to the $(3p_z)7_0^1$ transition. This resonance is shifted by 1468 cm^{-1} from the $(3p_x)0_0^0$ transition, and its photoelectron spectrum [Fig. 2(h)] shows an intense peak shifted by 191 meV (1541 cm^{-1}) from the $0''-0^+$ transition. Previous photoelectron spectra⁴¹ and our *ab initio* calculations (Table I) indicate that this peak corresponds with ionization to the $\nu_3^+ = 1$ level, which, in turn, implies that the resonance should be assigned to the $(3p_x)3_0^1$ transition. Peaks in the photoelectron spectrum shifted by 131 meV and 91 meV arise from ionization from levels associated with the $3p_y$ and $3p_z$ states.

The assignments as discussed above give evidence for various manifestations of vibronic coupling. In the case of the $3p_y$ state, interaction with the $\pi\pi^*$ valence state is not directly observed, but deduced, amongst else (*vide infra*), from the broadening of the two-photon resonances. Secondly, in the majority of the cases coupling occurs between a Franck–Condon allowed level and Franck–Condon forbidden levels on account of near-degeneracy, as a result of which the Franck–Condon forbidden transition obtains intensity in the excitation step, while in the photoionisation step the multistate description is dissected. Finally, Franck–Condon transitions are observed that do not become allowed by near-degeneracy of nontotally symmetric vibrational levels with allowed totally symmetric vibrational levels. These concern the transitions to a_2 vibrational levels of the $3p_x$ state, for example $(3p_x)12_0^1$, one transition to a b_1 vibrational level of this state, and transitions to b_2 vibrational levels of the $3p_z$ state. Although not seen in the present study, Kundu *et al.*¹³ previously also observed the extremely weak $(3p_x)24_0^1$ transition, i.e., a transition to a b_1 vibrational level of the $3p_x$ state. It has been suggested that for the $3p_x$ state a_2 modes might be particularly active because of the vibronic coupling that might occur then with the $\pi\pi^*$ valence state.¹⁴ The present results, in combination with the two-photon transition probability coefficients calculated by Galasso,⁵ give a strong indication that the dominant coupling routes concern vibronic coupling *within* the $3p$ Rydberg manifold. The calculations predict that the two-photon excitation cross section of the $3p_x$ and $3p_z$ states are of the same order of magnitude, while the one of the $3p_y$ state is an order of magnitude larger. The two-photon excitation cross-section of the $\pi\pi^*$ state is in-between those of the $3p_{x,z}$ and $3p_y$ states. Indeed, it is found that all three origin transitions have an intensity that is of the same order of magnitude, bearing in mind, however, that the origin transition to the $3p_y$ state is severely lifetime broadened. On the basis of these calculated numbers one would thus predict (i) that because of the small energy differences, $3p$ interstate coupling is more effective than coupling with valence states, and (ii) that $3p_x \leftrightarrow 3p_y$ and $3p_z \leftrightarrow 3p_y$ coupling would be more effective in inducing two-photon transition intensity than $3p_x \leftrightarrow 3p_z$ coupling, in perfect agreement with our observations of $(3p_x)(a_2)_0^1$ and $(3p_z)(b_2)_0^1$ transitions, and the extreme weakness of a $(3p_x)(b_1)_0^1$ transition.

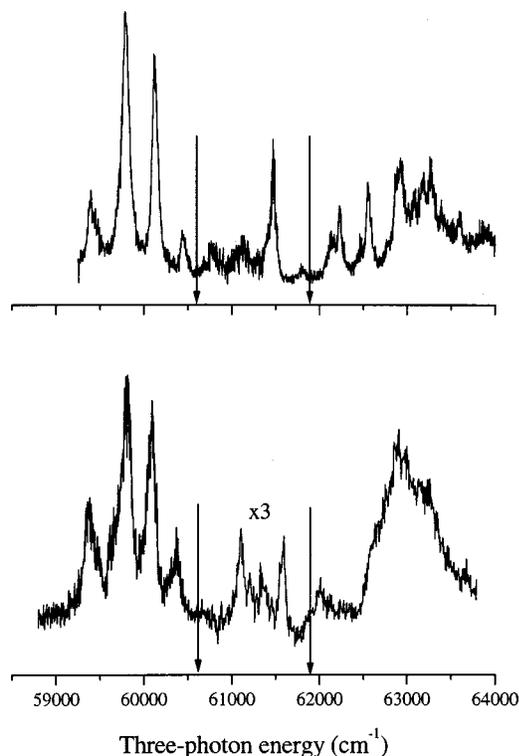


FIG. 5. (3+1) REMPI spectrum of room-temperature acetone- h_6 (top) and acetone- d_6 (bottom) in the region of 59 000–64 000 cm^{-1} . This spectrum is the composite of three different scans joint at the indicated excitation energies.

B. (3+1) REMPI-PES of acetone- h_6 and - d_6

The spectral region above the $3p$ states has in the past not been investigated extensively. A few experimental results concerning excitation above the $3p$ states have been reported by Merchan *et al.*,⁷ who investigated acetone- h_6 and - d_6 by jet-cooled (3+1) REMPI in the energy region of 7.7–8.3 eV. Here they assigned transitions to $3d$ Rydberg states. As was noticed previously¹¹ (1+2) ionization starts to interfere in this wavelength region, and we have therefore not pursued any additional two-photon excitation. In this section (3+1) REMPI results will be discussed that we have obtained in the energy region of 7.3–9.5 eV. The majority of these experiments have been performed under effusive conditions since previous experiments indicated that the widths of the three-photon resonances are significantly larger than the widths of the two-photon resonances, and that there is little to gain by performing jet-cooled experiments.

1. 58 500–64 200 cm^{-1} (7.2–7.9 eV) spectral region

This area contains the $3p$ region that has been extensively investigated by (2+1) REMPI in previous studies^{11,29} as well as in the previous section. The three-photon excitation spectra obtained with electron detection for acetone- h_6 under jet-cooled conditions and - d_6 under effusive conditions are shown in Fig. 5, and agree with those reported in previous work using ion detection. Figure 5 shows that—when compared to the 0–0 transitions to the two other $3p$ states—the 0–0 transition to the $3p_y$ state is relatively more intense than in the (2+1) REMPI spectrum. The higher laser inten-

sity required for (3+1) as compared to (2+1) multiphoton processes, advantages the ionization process when it is in competition with decay processes from the excited state. The change in relative intensities may thus be taken as further evidence for the short-lived nature of the $3p_y$ Rydberg state. Photoelectron spectra have been measured for various resonances of both acetone- h_6 and - d_6 and were found to confirm the assignments and conclusions reported in the previous section. The spectral region containing the high-energy part of the $3p$ excitation region that has not been investigated using two-photon excitation needs some further discussion.

For acetone- h_6 the $(3p_z)4_0^1$ transition was previously observed using two-photon excitation at 61 467 cm^{-1} , but for acetone- d_6 this transition was not reported. In the present (3+1) experiments we indeed observe and confirm with photoelectron spectroscopy this transition at 61 470 cm^{-1} , but moreover find that for acetone- d_6 the same transition occurs at 61 105 cm^{-1} , i.e., 1022 cm^{-1} shifted from the $3p_z$ origin. Ionization via this resonance leads to a photoelectron spectrum with an intense peak shifted by 127 meV (1024 cm^{-1}) from the $0''-0^+$ peak, in agreement with a $\nu_4^+=1$ assignment. Furthermore, a peak shifted by 216 meV (1742 cm^{-1}) is present that exactly matches the energy where one would expect a signal associated with ionization of a $3p_x$ vibrational level.

The peak in the excitation spectrum of acetone- d_6 at 61 327 cm^{-1} has neither been reported before. Ionization at this energy leads to the photoelectron spectrum displayed in Fig. 6(a) that has an intense peak shifted by 243 meV (1960 cm^{-1}) from the $0''-0^+$ peak. We assign this peak to the $\nu_5^+=2$ level because of the presence of a peak at 122 meV (984 cm^{-1}) that is assignable to $\nu_5^+=1$. On the basis of the excitation energy and this photoelectron spectrum, we conclude that the resonance should be assigned as the $(3p_x)5_0^2$ transition. Corroboration of this assignment is found in the presence of the $(3p_x)5_0^1$ transition in the (2+1) results. Peaks shifted by 154 and 194 meV in the photoelectron spectrum originate from coupling with the $3p_y$ and $3p_z$ states.

For acetone- h_6 vibronic transitions to CH stretch vibrational levels of the $3p$ Rydberg states would, energetically speaking, take place in the region around 62 250 cm^{-1} . It is good to realize that *a priori* one would not expect to see vibronic transitions to these kind of levels since that would imply that the geometry of the molecule changes along these vibrational coordinates. Since it is a nonbonding lone-pair electron, mainly localized on the oxygen atom, that is excited, it would be hard to rationalize such geometry changes. Moreover, if such transitions were visible in the excitation spectra of the $3p$ Rydberg states, one may expect the same Franck–Condon factors for ionization from the ground state, i.e., such transitions should then also appear in He(I) photoelectron spectra. Since this is not the case,⁴¹ any vibronic activity in this energy region points to an unusual situation.

Our (3+1) excitation spectrum displays two intense peaks at 62 241 and 62 559 cm^{-1} . Xing *et al.* reported a similar pair of transitions, shifted, however, by 50 cm^{-1} to the red (62 193 and 62 517 cm^{-1} , respectively).¹¹ Based on the spectra shown in Refs. 7 and 11, the energy difference between the two peaks, and the observed difference between

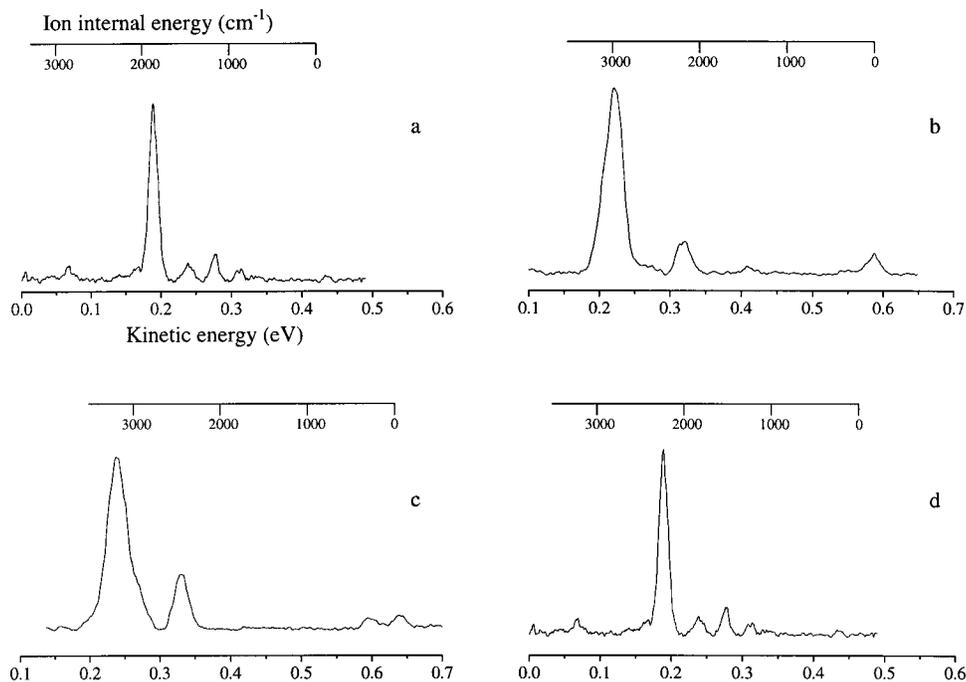


FIG. 6. (3+1) Photoelectron spectra of acetone- d_6 at (a) 61 327 cm^{-1} [$(3p_x)5_0^2$] and (d) 61 597 cm^{-1} [$(3p_y)2_0^1$], and of acetone- h_6 at (b) 62 241 cm^{-1} [$(3p_y)2_0^1$] and (c) 62 559 cm^{-1} [$(3p_y)2_0^1$].

jet-cooled and room-temperature excitation spectra, we assume that we deal here with the same transitions, and that the shift is only due to different experimental conditions. These resonances were previously assigned as a “local origin” and as the “local origin + ν_8 .”⁷ They concluded that this local origin corresponds to a vibrational subband of the $3p_y$ transition that has been enhanced by the energetically proximal 1A_1 ($\pi\pi^*$) valence transition. In the original three-photon excitation work¹¹ the local origin was assigned as the $(3p_y)2_0^1$ transition, but this assignment was not repeated in the subsequent study.⁷ The assignment to the $(3p_y)2_0^1$ transition implies that the frequency of the ν_2 vibration is reduced tremendously from 2937 cm^{-1} in the ground state to only 2425 cm^{-1} in the $3p_y$ state. This reduction was taken as evidence for a strong vibronic coupling between the $3p_y$ and the $\pi\pi^*$ excited states via ν_2 , which—since the $3p_y$ is the lower of the two states—would lead to a decrease of the frequency of ν_2 in the $3p_y$ state and a (nonconfirmed) increase in the $\pi\pi^*$ state.

The photoelectron spectrum obtained at 62 241 cm^{-1} [Fig. 6(b)] displays a small $0''-0^+$ peak and an intense peak, shifted by 368 meV (2947 cm^{-1}). The location of this peak would be consistent with the formation of ionization to the $\nu_2^+ = 1$ level (see Table I), and thus with an assignment of the resonance as $(3p_y)2_0^1$. There remains a catch, however, because the energy of 368 meV in the photoelectron spectrum matches also “exactly” the energy expected for ionization of a $3p_x$ vibrational level. Alternatively, one might therefore assign the resonance to excitation and ionization of a vibrational level of the $3p_x$ Rydberg state. The totally-symmetric nature of the transition¹¹ dictates, however, that the excited vibrational level is of A_2 symmetry. This implies (i) that the bright state in excitation is not that particular vibrational level of the $3p_x$ state, and (ii) that such a level has become accessible by vibronic coupling with the $3p_y$ state, which should thus be the bright state in excitation. One way to

reconcile these observations is to say that it is indeed the $(3p_y)2_0^1$ transition that provides the transition moment for excitation, but because of the short-lived nature of the $3p_y$ state—which will only be enhanced by the proximity of the $(3p_y)2_1^1$ level to the perturbing $\pi\pi^*$ state—the $3p_x$ state becomes the bright state in the ionization process. The photoelectron spectrum shows two additional peaks. The small peak, shifted by 175 meV (1411 cm^{-1}) from the $0''-0^+$ derives from ionization to the $\nu_4^+ = 1$ level, while coupling with the $3p_z$ state leads to the signal at 256 meV (2065 cm^{-1}).

The peak at 62 559 cm^{-1} in our acetone- h_6 excitation spectrum, previously assigned as “local origin + ν_8 ,”⁷ does not resolve this ambiguity. The associated photoelectron spectrum [Fig. 6(c)] displays a small peak shifted by 42 meV (341 cm^{-1}) from the $0''-0^+$ peak, consistent with formation of $\nu_8^+ = 1$ ions. The most intense peak is shifted by 400 meV (3230 cm^{-1}) and agrees both with ionization to the 2^18^1 ionic level and with ionization of a $3p_x$ vibrational level.

More information is obtained from the acetone- d_6 spectra. Here, a relatively intense resonance is observed at 61 597 cm^{-1} that is shifted by 2234 and 1762 cm^{-1} from the $3p_x$ and $3p_y$ origins, respectively. The strongest peak in the photoelectron spectrum [Fig. 6(d)] is shifted by 280 meV (2258 cm^{-1}) from the $0''-0^+$ peak. Table II indicates that this energy is at odds with a $\nu_2^+ = 1$ assignment, but agrees perfectly with the ionization signal of a $3p_x$ vibrational level expected at 278 meV from the $0''-0^+$ peak. This observation would thus favor the explanation based on the $(3p_y)2_1^1$ state being the bright state in excitation, and the coupled $3p_x$ state the bright state in ionization. Figure 6(d) displays two additional small bands shifted by 231 and 191 meV. The latter band agrees with the expected position for ionization of the $3p_z$ state (188 meV). The former band is assigned to ionization of $3p_y$ vibrational levels that are populated by IVR. This would account for the observed difference be-

TABLE V. Observed three-photon transitions to higher-lying Rydberg states of acetone- h_6 and $-d_6$.

acetone- h_6		acetone- d_6		Assignment
$\bar{\nu}$ (cm^{-1})	($n-\delta$)	$\bar{\nu}$ (cm^{-1})	($n-\delta$)	
65 250		65 325	2.91	$3d_{x^2-y^2}(^1B_2) 0_0^0$
65 628		65 604		$3d_{x^2-y^2} 8_0^1$
65 910	2.98	65 865	2.97	$3d_{xy}(^1B_1) 0_0^0$
		66 159		$3d_{x^2-y^2} 6_0^1$
		68 961	3.43	$4p_x(^1A_2) 0_0^0$
		69 339	3.50	$4p_z(^1B_2) 0_0^0$
		70 041		$4p_x 4_0^1$
71 553	4.03	71 511	4.02	$4d 0_0^0$
71 890	4.14	71 835	4.12	$5s 0_0^0$
73 902	4.98	73 844	4.96	$5d 0_0^0$
74 170	5.15	74 145	5.14	$6s 0_0^0$
75 258	6.01	75 208	5.97	$6d 0_0^0$
75 420	6.17	75 384	6.13	$7s 0_0^0$
76 068	7.01	76 017	6.93	$7d 0_0^0$
76 176	7.19	76 134	7.12	$8s 0_0^0$

tween the 1762 cm^{-1} (218 meV) spacing in excitation and the 231 meV spacing in the photoelectron spectrum.

2. 65 000–71 000 cm^{-1} (8.0–8.8 eV) spectral region

For excitation energies superseding the $3p$ Rydberg states the signals decrease dramatically in intensity, and it is not always possible to obtain excitation and photoelectron spectra under jet-cooled conditions with a sufficient signal to noise ratio to allow their detailed analysis. We have therefore recorded in most cases spectra under both jet-cooled as well as effusive conditions. As indicated already previously, three-photon excitation itself leads to rather broad resonances. The difference in resolution between jet-cooled and effusive conditions is therefore generally not dramatic. Resonances found in this energy region are tabulated in Table V.

This part of the spectrum is dominated by two peaks found at $65\,250$ and $65\,910 \text{ cm}^{-1}$ in acetone- h_6 , and $65\,325$ and $65\,865 \text{ cm}^{-1}$ in $-d_6$. Previous (3+1) REMPI experiments located the three-photon origin transitions to the $3d_{x^2-y^2}(^3B_2)$ and $3d_{xy}(^2B_1)$ Rydberg states at $65\,293$ and $65\,944 \text{ cm}^{-1}$ ($65\,352$ and $65\,987 \text{ cm}^{-1}$ for $-d_6$), respectively.⁷ Compared to these numbers, we thus find here for acetone- h_6 red-shifts of 43 and 34 cm^{-1} , respectively, that are probably caused by the different experimental conditions, and the fact that the resonances are rather broad. Indeed, photoelectron spectra recorded at these resonances confirm that they concern 0–0 transitions. As is by now expected, the photoelectron spectra also show that the states are extensively coupled to the lower-lying $3p$ Rydberg states. The vibrational development is rather restricted: for acetone- h_6 we find and confirm by photoelectron spectroscopy the previously proposed ($3d_{x^2-y^2}$) 8_0^1 transition at $65\,628 \text{ cm}^{-1}$, for acetone- d_6 the ($3d_{x^2-y^2}$) 8_0^1 transition at $65\,604 \text{ cm}^{-1}$ and the ($3d_{x^2-y^2}$) 6_0^1 transition at $66\,159 \text{ cm}^{-1}$.

The quantum defects of the $3p$ states lead us to expect transitions to the $4p$ states to occur around $69\,000 \text{ cm}^{-1}$. Indeed, for acetone- h_6 two origin transitions have previously been assigned at $68\,999$ and $69\,348 \text{ cm}^{-1}$, respectively,⁷

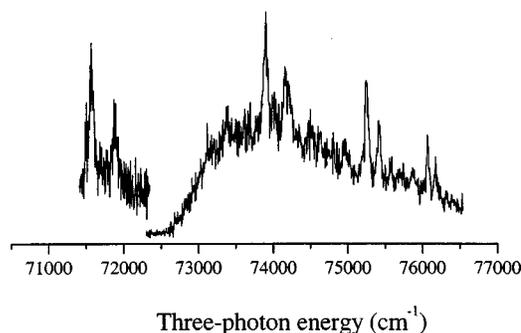


FIG. 7. (3+1) REMPI spectrum of room-temperature acetone- h_6 in the region of $71\,000$ – $76\,500 \text{ cm}^{-1}$. The spectrum has been obtained employing two different dyes in the two indicated scans.

while for acetone- d_6 these transitions were located at $68\,793$ and $69\,350 \text{ cm}^{-1}$. In the present study the transitions in this spectral region were so weak for acetone- h_6 that neither under jet-cooled, nor under effusive conditions a decent excitation spectrum could be obtained. For acetone- d_6 , on the other hand, the (3+1) REMPI spectrum showed distinct peaks at $68\,961$ and $69\,339 \text{ cm}^{-1}$ for which photoelectron spectra indicated that they should be assigned as origin transitions. In passing by, we notice that also in the three-photon excitation study of Merchan *et al.*⁷ the reported acetone- h_6 spectrum had a significant lower signal to noise ratio in this region than the $-d_6$ spectrum. These transitions most logically would be assigned to the two $4p$ states assigned previously, were it not that the transition at $68\,961 \text{ cm}^{-1}$ seems rather much displaced from the reported value of $68\,793 \text{ cm}^{-1}$.⁵ *A posteriori* we notice, however, that the values of Merchan *et al.* imply a negative isotope shift of 206 cm^{-1} for the $68\,999 \text{ cm}^{-1}$ transition, which is at odds with the values of isotope shifts of the other transitions observed so far: apart from a small negative value for the $3p_z$ excitation, only positive values were found. The transition energy of $68\,793 \text{ cm}^{-1}$ is therefore most likely incorrectly reported.

Comparison with the splittings in the $3p$ manifold enables us to assign the two origin transitions. The energy difference between them is 378 cm^{-1} and is expected to be roughly proportional to $1/n^3$. That means that an analogous energy difference of around 1000 cm^{-1} can be expected in the $3p$ manifold. The two Rydberg states having an energy difference that comes close to this value are the $3p_x$ and $3p_z$ Rydberg states. An additional argument for the implied non-observability of the $4p_y$ Rydberg state is that we can expect this state to be short-lived on account of its coupling with the $\pi\pi^*$ state. These arguments strongly favor an assignment of the peaks at $68\,961$ and $69\,339 \text{ cm}^{-1}$ to the $4p_x$ and $4p_z$ Rydberg states, respectively.

3. 71 000–76 500 cm^{-1} (8.8–9.5 eV) spectral region

The jet-cooled (3+1) REMPI spectrum of acetone- h_6 in the spectral region of $71\,000$ – $76\,500 \text{ cm}^{-1}$ is shown in Fig. 7. In order to have sufficient signal intensity, the spectrum was recorded in the two indicated scans using Exalite 416 and 404 for the $71\,500$ – $72\,500$ and $72\,500$ – $76\,500 \text{ cm}^{-1}$ regions, respectively. Efforts to record spectra between

72 000 and 73 500 cm^{-1} with Exalite 411 were not successful due to low dye gain. An analogous spectrum (not shown) was obtained for acetone- d_6 . Effusive (3 + 1) REMPI spectra show similar results, albeit that the maxima of the peaks are shifted by 30–40 cm^{-1} to the red. The spectra show eight resonances whose positions are given in Table V. The resonances observed in the present study match well peaks observed in previous one-photon work,³¹ although in that work an assignment was not attempted.

Because of the low signal intensities, photoelectron spectra have been recorded under effusive conditions. These spectra demonstrate that the resonances are associated with origin transitions. In general, the photoelectron spectra show that the states excited at these energies are subject to extensive coupling with lower lying Rydberg states. An example is shown in Fig. 8, where ionization occurs via the resonance assigned to the 6*d* manifold. Apart from ionization to the vibrationless level of the ion, extensive ionization occurs to high vibrational ionic levels. Under the assumption of a $\Delta v = 0$ ionization behavior, we can calculate what excitation energy is associated with each peak in the photoelectron spectrum. As indicated in Fig. 8, these excitation energies agree well with the excitation energies of Rydberg states determined previously and in the present study. Apart from states that were already known, the photoelectron spectra also enable us to observe and assign states that we have not observed as resonances in the excitation spectra—in this particular case, for example, the 5*p* Rydberg states.

Calculation of the quantum defect associated with each of the observed transitions in the excitation spectrum leads to the conclusion that members are observed of two Rydberg series with quantum defects of approximately 0 and 0.85. The first series can be grouped nicely with the ${}^1B_1(n \rightarrow 3d_{xy})$ transition observed at 65 910 cm^{-1} , and allows us to conclude that this concerns an *nd* Rydberg series of which we have now identified the $n=3-7$ members. The second series is assigned to the *ns* series, of which the first member is the in the introduction mentioned 3*s* state located at 51 232 cm^{-1} . The states excited in the present experiments are described by the excitation of an electron from the non-bonding lone pair orbital that in first approximation can be represented by the 2*p_y* orbital on the oxygen atom. Atomic selection rules then dictate a $\Delta l = \pm 1$ propensity for one-photon excitation, and a $\Delta l = \pm 1, \pm 3$ propensity for three-photon excitation. The present assignment to *ns* and *nd* Rydberg states is thus in good agreement with such expectations.

IV. CONCLUSIONS

The application of photoelectron spectroscopy to characterize excited states of acetone- h_6 and - d_6 has led to a detailed picture of the spectroscopic properties of excited states of acetone, and of some vibrational properties of the ground state of the radical cation. In particular for the 3*p* Rydberg states, the present study has modified and extended assignments proposed in previous multiphoton ionization studies. Apart from the characterization of previously observed states, some eight new Rydberg states have been identified and studied. The observed photoelectron spectra give in all

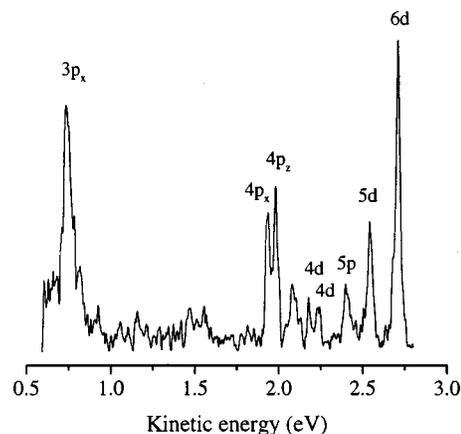


FIG. 8. (3 + 1) Photoelectron spectrum of acetone- h_6 via the 0–0 transition to the 6*d* Rydberg state at 75 258 cm^{-1} .

cases evidence for an important role of vibronic coupling in determining the observable spectroscopic properties of the excited states under investigation. This has been exemplified to the extreme for 3*p* Rydberg states where the state that is excited in the multiphoton excitation process could be projected on the basis of the 3*p_x*, 3*p_y*, and 3*p_z* states. One of the dominating coupling pathways, which is not directly visible in the photoelectrons spectra, but can be deduced from the combination of excitation and ionization properties of excited states, is that between the $\pi\pi^*$ (1A_1) excited valence state and Rydberg states of A_1 symmetry. Because of the short-lived nature of the former state, Rydberg states of A_1 symmetry lose intensity in excitation and ionization, but ultimately reveal themselves once again by vibronic coupling with longer-lived Rydberg states. Although vibronic coupling of the $\pi\pi^*$ excited valence state with Rydberg states of other symmetries is theoretically possible, it has been shown that for these states other vibronic couplings prevail. These pathways do become nicely visible in the photoelectron spectra and concern the intra-, e.g., between the 3*p* components, and interstate, e.g., between 7*d* and 3*p*, couplings between all other Rydberg states. Because of this coupling, excitation energies of states that were not visible in our excitation spectra, e.g., the 4*p* and 5*p* Rydberg states, could be determined from photoelectron spectra taken at higher excitation energies.

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