

Angular momentum coupling in molecular Rydberg states

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Abstract - The coupling of electronic and nuclear motions in the rovibronic levels of the lowest Rydberg states of methyl iodide is discussed in terms of a frame transformation between lab- and body-frame coordinate systems for an s Rydberg electron in the field of an electronically-degenerate, symmetric-top molecular ion core. It is shown that the r-dependence of exchange, spin-orbit, spin-rotation, and vibronic interactions, where r is the radial distance of the electron from the ion core, must be considered in order to provide a consistent analysis of the experimental data. Molecular constants, obtained by fitting one- and two-photon absorption spectra, show conclusively that the spin of the Rydberg electron is uncoupled from the molecular frame. Bandshape fitting reveals that the interaction between electronic and vibrational angular momenta leads to complete angular momentum quenching in some vibronic levels, in which it appears that the vibrating core "traps" the Rydberg electron. The magnitudes of the B rotational constants permit extrapolation of channel mixing across ionization thresholds in CH₃I but not in HI. A theoretical frame for the discussion of these events is sketched.

A. INTRODUCTION

This paper is the latest of a series¹⁻⁷ which attempts to apply multichannel quantum defect theory⁸⁻¹⁰ (MQDT), the frame transformation aspect of it, or both, to polyatomic systems. QDT procedures have been successfully applied to a variety of problems in atoms^{9,11} and diatomics¹², but progress for polyatomics has come very slowly. In this work, we will be concerned with a very limited portion of the VUV spectrum of methyl iodide (i.e., the 6sR, or lowest s Rydberg region), and we will focus on a particular ingredient of MQDT, namely frame transformations^{10,11}.

The wavefunction of a Rydberg electron with low angular momentum extends over small-r and large-r regions, where different physical situations prevail⁸. The descriptions of the system in these two regions, in terms of alternative expansions of the total wavefunction, are related by a transformation of the orbital and spin coordinates of the Rydberg electron from a molecule-fixed coordinate system, in which the initial photoabsorption event occurs, to a laboratory frame coordinate system, one more convenient for representing the motions of a spatially-extended Rydberg electron. Most discussions of polyatomic Rydberg states have emphasized the large-r character of the electron orbital and neglected small-r, off-diagonal effects which mix different electronic, vibrational and rotational channels.

The purpose of this work is to develop frame transformation theory for a Rydberg electron in the field of an electronically-degenerate, symmetric-top molecular ion core, and to use it to classify rovibronic Rydberg states. The choice of the lowest Rydberg states of CH₃I is convenient because these states are more or less uncontaminated by valence states and are so isolated from higher Rydberg members that the multichannel aspects of ℓ -mixing can be neglected. Furthermore, because of the strong internal spin-orbit coupling in the ion core, Jahn-Teller distortions will be negligible. On the other hand, intraconfigurational mixing induced by spin-orbit, exchange, and the nuclear kinetic energy terms will be found to be significant.

Methyl iodide, since the early days of molecular spectroscopy, has been a focus of molecular UV and VUV studies, yet much of its more interesting physics remains to be uncovered. It is hoped that our discussion of rovibronic effects will facilitate continued probing of these Rydberg manifolds.

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It is now appropriate to summarize the observations/deductions about the Rydberg manifold of CH_3I that speak to MQDT and/or transformation theory. These are:

1. The frame transformation method has been applied¹ to the rotational band shape analyses of one-⁵ and two-photon⁶ 6sR absorption spectra of CH_3I . It has been shown that uncoupling of spin angular momentum of the optical electron from the molecular axis was essentially complete. The same result may be deduced² from an empirical correlation of the entire experimental data set.
2. It has been shown that the 6sR photoabsorption event must be viewed as a two-step process³: In the first, the initial electronic excitation accords with the Born-Oppenheimer Approximation (BOA), while the second consists of angular uncoupling of the Rydberg electron as it escapes from the rotating molecular core.
3. An MQDT analysis of the high-resolution absorption spectrum of CH_3I has been performed⁴ for energy regions above and below the first ionization limit. It has been shown that spin-orbit coupling and ℓ -mixing of Rydberg states built on a doublet ion core account for nearly all major aspects of the spectrum. The ability to extrapolate channel mixing in CH_3I across threshold from the autoionization region to the discrete region, and the inability to do so in HI, is attributable to the much smaller value of the B rotational constant for CH_3I .
4. Nuclear-electronic coupling was observed^{1,5,6,7} in the ν_6 vibronic bands of CH_3I that are built on the 6sR origins. This coupling produced⁷ almost complete quenching of angular momentum in some such levels.
5. The vibrating nuclear frame (ν_6 mode, as discussed above) increases the region of the electron core/optical electron interactions to larger radial distances. It appears⁷ that the vibrating core "traps" the Rydberg electron.
6. A transference of angular momentum between other, almost degenerate vibronic pairs has also been observed⁷. It was shown that the coupling operator was rovibronic, the most important part of it being analogous to the Renner effect in linear molecules. However, because of the importance of Coriolis coupling in the non-linear, symmetric top molecule CH_3I , this vibronic, Renner-like part does possess first-order effects.
7. Valence/Rydberg interactions were observed on both sides of the ionization limit(s) and were interpreted. These interactions, while extensive and solely responsible for the photochemistry associated with Rydberg excitations below the first ionization limit, do not vitiate any of the above conclusions/deductions.

The emphasis of the present work resides in statements 1, 2, 4, 5 and 6. Connections to statements 3 and 7 obviously exist, but these connections will not be explored in detail.

B. ROTATIONAL-ELECTRONIC STRUCTURE OF THE 6sR ORIGIN BANDS

The electronic structure of the 6sR states of methyl iodide was first elucidated by Mulliken^{13,14,15}. These states are formed by promotion of an electron from the filled 2e orbital (essentially a nonbonding iodine AO) to the Rydberg 6s (6sR) orbital¹⁶. Term symbols and energies of the 6sR states are listed in Table 1. Herzberg¹⁷ discussed the splittings of this configuration in the (Λ, S) and (Ω_C, ω) electronic coupling limits, where Λ and S denote the projections of the total orbital and total spin electronic angular momenta onto the molecular axis; Ω_C refers to the same projection of the total (orbital plus spin) electronic angular momentum of the core electrons and ω specifies the same projection of the total angular momentum of the Rydberg electron. The characteristic features of the CH_3I photoabsorption spectrum are:

- 6sR configurational splittings are quantitatively described by spin-orbit, spin-spin and exchange interaction energies.
- The importance of the static Jahn-Teller effect to vibronic structure depends on the strength of spin-orbit coupling and varies inversely with the splitting of core degeneracy. First-order vibronic distortions, therefore, are minimal, and a C_{3v} molecular symmetry group is appropriate for classification of the rovibronic levels.
- The rotational envelopes of the 6sR origin bands are not much broadened by predissociative Rydberg-valence interactions. Indeed, the half-bandwidths are consistent with the assumption of small differences in the moments of inertia of upper and lower states.
- The molecular constants for the 6sR states are given in Table 2. The results of Table 2 differ substantially from those of Herzberg¹⁷, Mulliken and Teller¹³, and Parker et al.¹⁸.

The very different values we report for the rotational constants A and the effective internal angular momentum ζ_{eff} arise because the possibility of a spin uncoupling of the Rydberg electron from the molecular axis had not been considered previously.

- The Born-Oppenheimer Approximation (BOA) is inapplicable to the 6sR states of the rotating molecule: the spin projection of the 6sR electron ceases to be a good quantum number, because of the short-range nature of exchange, outside the core. While the energy spacing of electronic origins can be fully understood within the BOA [i.e., as coupling intermediate to the (Λ, S) and (Λ_c, w) limits], the form of the final-state angular momentum must be explicitly included in order to interpret the rotational fine structure of the 6sR bands.

C. FRAME TRANSFORMATION RELATIONS

A frame transformation relation connects alternative expansions of the full wavefunction constructed in different regions of molecular configuration space. The most familiar example is the intermediate coupling^{10,11} lying between the various Hund's cases for a diatomic. The appropriate partitioning of the configuration space of a homonuclear diatomic was depicted schematically in Fig. 1 of Chang and Fano¹¹ and is represented by bracketed quantum numbers in Fig. 1 of the present article. The quantum numbers for a symmetric-top are also shown in Fig. 1. An explication of Fig. 1 proceeds as follows:

- Global quantum numbers are given on line a). Lines b)-d) represent various local (approximate) solution of the full Hamiltonian. Roelectronic mixing is shown on line b). Additional effects induced by vibronic interactions are depicted on line d). Long-range orbital angular momentum coupling is represented on line c).
- Rotational analysis of the 6sR origin bands provides information about the coupling represented on line b) for a pure s electron. Analysis of the 6sR vibronic bands leads to information about the coupling indicated on lines b) and d), namely the effect of nuclear vibrations on the escape of the Rydberg electron from the region $r < r_0$. Because r_1 extends beyond the core, rotational constants for the vibronic transitions may differ from those of the origin band because of the nature of their angular momentum coupling.
- Beyond the 6sR region (i.e., for $E > 58000\text{cm}^{-1}$), the spectrum is complicated by Rydberg-Rydberg and Rydberg-valence interactions. The regular Rydberg progressions beginning about 74000cm^{-1} can now be modeled by MQDT parametrization of the long-range orbital angular momentum coupling. The range of this coupling is indicated by the boundary r_2 .
- Between 58000cm^{-1} and 75000cm^{-1} , Rydberg-valence interactions exert substantial effects on Rydberg series members. The generalized MQDT approach of Guisti¹⁹ suggests that the underlying valence states of the molecule may be probed by this technique.

The frame transformation is diagonal in the rovibronic quantum number²⁰ G and the total angular momentum J of the system. Various local quantum numbers of the region A (region B) descriptions of Fig. 1, which describe the small- r (large- r) behavior of the molecular complex (fragments), are determined by separation of the full Hamiltonian (see Appendix). The Chang-Fano formulation of the frame transformation matrix for a homonuclear diatomic¹¹ is readily generalized to an s Rydberg of a symmetric-top molecule by introducing restrictions on the values of the symmetric-top quantum numbers K_c and K , where K_c (K) represents the projection of the total angular momentum onto the molecular axis for the ion core (molecular complex), which can enter into the vector coupling coefficients. These additional selection rules are important to a correct accounting of the uncoupling of 6sR angular momentum from the molecular axis in the presence of first-order Coriolis coupling: It is necessary to distinguish the direction of rotation about the molecular axis for the sum of the electronic and nuclear angular momentum vectors. For example, for the case of an s-electron:

$$K_c = K \pm 1/2 = \pm \Omega \pm k \pm 1/2 \quad (1)$$

This "bookkeeping" is conveniently handled by the quantum number G .

According to line b) of Fig. 1, the spin projection of the 6sR electron on the molecular axis is only meaningful when $r < r_0$. In this region, an intermediate coupling description of the electronic angular momentum is required since spin-orbit coupling and exchange terms are both large. The local rotational-electronic quantum numbers for region A are given by the sets

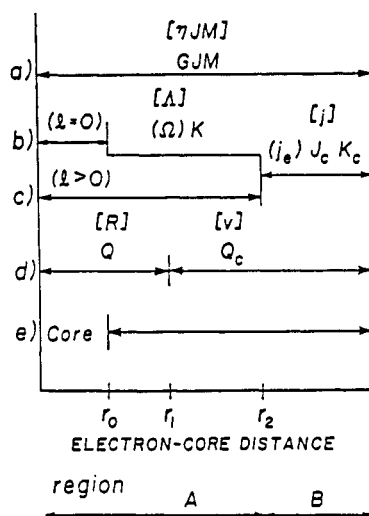
TABLE 1. Symmetry species, energies and quantum defects for the ground state and electronic states of the $6s a_1$ Rydberg configuration of CH_3I .

STATE #	SYMMETRY SPECIES			ENERGY (cm^{-1})	QUANTUM DEFECT $\mu(\text{IP})^c$
	$C_{\infty v}$	C_{3v}^a	C_{3v}^b		
0	$1\Sigma^+(0^+)$	A_1	-	0	-
1	$3\Pi(2)$	E	$6s; 2E_{3/2}$	49201	4.010(I_1)
2	$3\Pi(1)$	E	$6s; 2E_{3/2}$	49715	3.992(I_1)
3	$3\Pi(0\pm)$	A_1, A_2	$6s; 2E_{1/2}$	54030	4.017(I_2)
4	$1\Pi(1)$	E	$6s; 2E_{1/2}$	54640	3.997(I_2)

a) In a (Λ, S) coupling limit.b) In a (Ω, ω) coupling limit.c) Relative to the $2E_{3/2}(I_1)$ or $2E_{1/2}(I_2)$ ion core limits of CH_3I^+ .TABLE 2. Molecular constants^{4, 5, 6} of the $6sR$ electronic levels of CH_3I .

STATE #	ROTATIONAL CONSTANTS (cm^{-1})		INTERNAL ANGULAR MOMENTUM ζ_{eff}
	A	B	
0	5.119	0.250	0
1	4.343	0.245	1.40
2	4.446	0.245	1.30
3	4.906	0.245	0.70
4	5.008	0.240	0.65

a) All excited-state values are correct to about 5%. The ground state constants are taken from Ref. 17.

Figure 1. Diagram showing quantum numbers for a symmetric top molecule for different ranges of the electron-core distance r . Quantum numbers in brackets relate to a homopolar diatomic and are those given in Fig. 1 of Ref. 11. See text for definitions of symbols and different coupling regions.

$$\{\alpha\} = \{\Omega(\Lambda, S), K\}; \{\bar{\alpha}\} = \{\Omega(\Omega_c, \omega), K\} \quad (2)$$

in which the idealized electronic angular momentum coupling schemes are given as well. Spin-orbit coupling is a purely electronic component of the overall frame transformation matrix elements:

$$\langle \alpha | \bar{\alpha} \rangle = \langle \Lambda, S | \Omega_c, \omega \rangle. \quad (3)$$

The region B description, on the other hand, corresponds to a situation in which the orbital and spin coordinates of the Rydberg electron refer to a lab frame system. The quantum numbers for a $6sR$ state in this representation are

$$\{i\} = \{s, \Omega_c, K_c, J_c\} \quad (4)$$

where s is the spin of the Rydberg electron and Ω_c , K_c and J_c are core variables.

The overall frame transformation connecting regions A and B, which is denoted $\langle i | \alpha \rangle^{GJ}$, cannot be constructed by simply letting $k \rightarrow K_c$ (i.e., independently of the values of Ω and Ω_c). First-order Coriolis coupling is significant in both the molecular complex and the ion core and this coupling spoils the usefulness of the individual rotational and electronic quantum numbers K , Ω and Ω_c as the system evolves from region A to region B. For region A, the projection of the total angular momentum on the molecular axis is

$$K = k + \zeta_{\text{eff}}, \quad (5)$$

where ζ_{eff} , in the absence of vibronic coupling, is

$$\zeta_{\text{eff}} \leq \Omega \left| \frac{L+S}{2} \right| \Omega \quad (6)$$

because $\overline{(L+S)^2} = \overline{(L+S)^2} = 0$. The projection of the total angular momentum on the molecular axis \bar{x} of the molecular ion core in region B is given by a similar expression, namely

$$K_c = k + \zeta_{\text{eff}}^+ \quad (7)$$

and is related to the K levels of the molecular complex by Eq. 1. The quantity ζ_{eff}^+ is given approximately by $\Omega_c = 3/2, 1/2$.

Hougen²⁰ noted the invariance of the total wavefunction of a symmetric-top molecule to permutations of identical nuclei and used it to classify their rovibronic levels. Thus, the quantum number²¹ G is a bookkeeping device for the direction of the total electronic (G_e), vibrational (G_v), and rotational (k) angular momenta about the symmetry axis:

$$G = G_e + G_v - k \quad (8)$$

G has the advantage that it is conserved during the initial, purely electronic stage of photoabsorption and during the uncoupling of the molecular complex into the final states. Again following Hougen²⁰, it is convenient to specify degenerate pairs of roelectronic levels by

$$G_a = \pm (|G_e| - k) \quad (9a)$$

$$G_b = \pm (|G_e| + k). \quad (9b)$$

The selection rules for G are represented here by $\langle G \rangle$, where

$$\langle G \rangle = 1, \text{ if } G_a = G_a^+ \text{ or } G_b = G_b^+; \langle G \rangle = 0, \text{ otherwise} \quad (10)$$

and where the symbols G_a^+ and G_b^+ label the rovibronic levels of the freely rotating molecular ion core. The overall frame transformation for the 6sR states then becomes

$$\langle i | \alpha \rangle^{GJ} = [(2J_c + 1)/(2J + 1)]^{1/2} (1/2\Omega_c J_c K_c | 1/2J_c JK) \langle i | \alpha \rangle \langle G \rangle \quad (11)$$

The part of the spin uncoupling operator that is of interest here induces mixing, as in a diatomic molecule, by "end over end" rotations. Thus, the off-diagonal matrix elements in the region A representation are

$$\langle \chi^\alpha | V_{JS} | \chi^{\alpha'} \rangle = (1/2) \langle \chi^\alpha | J_+ S_- + J_- S_+ | \chi^{\alpha'} \rangle \quad (12)$$

where χ^α is a function of all electronic and nuclear coordinates except for the radial distance r of the Rydberg electron¹¹.

Resolution of the $J \cdot S$ operator in C_{3v} reveals²² that the species $(J_+ \square S_+)$ possess E symmetry. This leads to the following selection rules for Σ , the projection of the total spin on the molecular axis, and K :

$$\Delta\Sigma = \pm 1; \Delta K = \pm 1 \quad (13)$$

Setting $K = k + \zeta_{eff}$, as before, the selection rules may be rewritten as either

$$\Delta\Omega = \pm 1 \text{ and } \Delta k = 0 \quad (14)$$

where no change occurs in the nuclear rotational quantum number k or as the alternate possibility

$$\Delta\Omega = 0 \text{ and } \Delta k = \pm 1, \quad (15)$$

where the rotational quantum number changes by unity. Note that Eq. 14 is a familiar result in diatomic spectroscopy but that Eq. 15 has no such counterpart because, for a diatomic, $K \equiv \Omega$.

D. CLASSIFICATION OF ROVIBRONIC LEVELS

A set of correlation diagrams, one for state 2 and one for state 3, is given in Figs. 2a,b. These correlation diagrams are vested in the discussion of the previous section and will be discussed in some detail. In the discussion of Figs. 2a,b, we will distinguish the values of k in regions A and B by k' and k'' , respectively. We impose this distinction because the possibility of a slight zero-point shift of the levels, attributable to spin contributions, should occur.

The empirical parameters of bandshape fittings^{1 7} are the rotational constants, A and B , and the internal angular momentum, ζ_{eff} . These parameters, for a given rotational envelope, are obtained from the oscillator strength distribution and the energy spacing of the sub-bands. The sub-band spacing is given by the difference between $2A\zeta_{eff}$ for the upper and lower states of the rotational term energy. Since only the product $A\zeta_{eff}$ can be determined from a single band, care must be exercised in the assignment of individual values to A and ζ_{eff} . Experience, however, shows that the calculated spectrum is extremely sensitive to small parameter variations in certain neighborhoods of ζ_{eff} and A whereas, in other neighborhoods, there is much insensitivity to such variations. Such an insensitive region occurs for $\zeta_{eff} = 1$ and $A'' \sim A'$, where A'' and A' are the upper and lower state constants.

Rovibronic core levels in the region B representation are associated with half integer angular momenta. Since these levels correlate with integer-valued K levels in the region A representation, as shown in Figs. 2a,b, consistency with conservation of G must be maintained. The following comments are pertinent to the construction of Fig. 2.

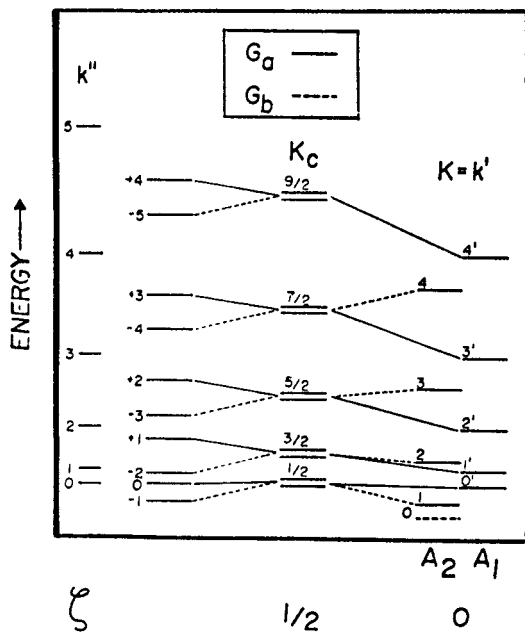
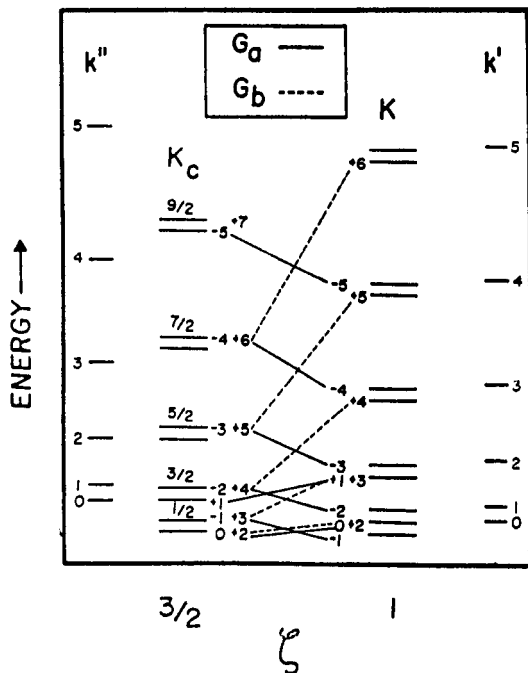


Figure 2. Correlation diagrams for the roelectronic levels of a symmetric top molecule in which both Coriolis and spin uncoupling are important.

a) Diagram for state 2 of the 6sR configuration of CH_3I . k' and k'' are quantum numbers for pure nuclear rotation about the molecular axis in regions A and B, respectively. K and K_c are projections of the total angular momentum on the molecular axis when the spin of the Rydberg electron is alternately referred to the body frame and lab frame, respectively; and G_a and G_b are rovibronic quantum numbers for classifying levels of the symmetric top. The K quantum number has been omitted for reasons of clarity; the correlation lines indicating Coriolis splitting of the k' and k'' levels have also been left out. The energy level spacings are roughly to scale.

b) Uncoupling diagram for the A_1 and A_2 components of state 3 of the 6sR configuration.

- k' and k'' are the (zero-order) quantum numbers for nuclear rotation in regions A and B.
- The G_a and G_b quantum numbers occur in Fig. 2a in the region between $3/2 < \zeta < 1$; in Fig. 2b, they occur to the left of the levels for which $\zeta > 1/2$.
- Selection rules pertaining to the spin-uncoupling operator were used in making the correlations.
- The full spin degeneracy of the region B levels (i.e., Kramer's degeneracy) is not shown.
- Individual J levels are not shown because they do not influence the classification scheme.
- The K quantum numbers for the individual levels of the region A description and the doubled nature of the k levels have been omitted for clarity.
- Fig. 2a was constructed for state 2 but is equally pertinent to state 1 with slight alternations of the K level spacing. Indeed, since bandshape calculations show that $\zeta_{\text{eff}} \sim 3/2$ for both states, a separate diagram is superfluous.
- Mixing of different electronic states $\Omega = 2, 1, 0$, and 1 is not shown. This is equivalent to setting $\langle i | \alpha \rangle = 1$ in Eq. 11.

If the spin of the Rydberg electron remained coupled to the molecular axis, as was previously assumed, the mixing of singlet and triplet wavefunctions by the spin-orbit operator would be essentially complete and would yield

$$\begin{aligned}\chi_2(\Omega = 1) &= 2^{-\frac{1}{2}}[\phi(^3\Pi_1) + \phi(^1\Pi_1)] \\ \chi_4(\Omega = 1) &= 2^{-\frac{1}{2}}[\phi(^3\Pi_1) - \phi(^1\Pi_1)]\end{aligned}\quad (16)$$

Such complete mixing implies that both states should possess identical rotational envelopes. Since the observed bandshapes are very different in both the one- and two-photon spectra, it is quite clear that the rotational structure of the 6sR states of CH_3I cannot vest solely in a BOA approach.

E. DISCUSSION

The method of frame transformations¹⁰ has been applied here to spin uncoupling in Rydberg states of a symmetric-top molecule. The utility of this approach is amply justified by the bandshape simulations of one- and two-photon spectra given by Dagata and McGlynn¹⁻⁵. Indeed, in retrospect, it is surprising that BOA breakdown for these isolated s Rydbergs should have escaped attention for so long. It turns out that the effects of spin uncoupling are rather subtle in the one-photon absorption spectra, seeming to confer properties associable with modified vibrations. This latter statement is a consequence of the fact that region A extends to $r > r_0$ when vibrations are excited. Since the analyses of Mulliken and Teller¹³, and Herzberg¹⁷ were limited to the extraction of rotational constants from the sub-band spacing of vibrationally degenerate vibronic levels (i.e., the so-called widely-spaced bands), and since these data were not inconsistent with BOA, it was believed that the 6sR states of CH_3I were well understood. It was not until two-photon resonant MPI studies¹⁸ became available that inconsistency was exposed^{5,6,7}.

An important connection exists between the application of rotational frame transformations to the 6sR states¹⁻⁷ and the recent application⁵ of full MQDT procedures to the high-lying Rydberg levels in the "discrete" and autoionizing regions near the first ionization threshold of CH_3I . Unlike the electronically-similar diatomic HI, rotational-electronic mixing is suppressed by the smallness of the B rotational constant of methyl iodide. Furthermore, Coriolis coupling effectively superposes all the symmetric-top rotational sub-bands at or near the band origin. It is then easy to associate band maxima at very high n with a unique electronic origin. Consequently, it was possible to unravel major portions of the discrete and autoionizing regions of CH_3I using *ab initio* MQDT parameters²³ for HI. Similar transference across I_1 , however, was not feasible in HI itself!

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APPENDIX

The QDT approach emphasizes the radial motion of the Rydberg electron outside the core region, $r > r_2$. The fragmentation channels are specified by a set of quantum numbers $\{i\}$. The net effect of the short-range electron-core interactions for a given eigenchannel α of the molecular complex outside the core boundary is represented by a quantum defect parameter, μ_α . If the number of fragmentation channels n_i is greater than one, then the frame transformation relation $\langle i | \alpha \rangle$ must be constructed.

In this Appendix, we obtain the relevant short-range interactions by writing the full Hamiltonian

$$H = H_0 + V \quad (A1)$$

in terms of a zero-order Hamiltonian of the form

$$H_0 = H_c + h(r) = [(T_N^+ + T_e^+ + V^+)_{\text{core}} + h(\hat{r})] + h(r) \quad (A2)$$

where the terms $(\dots)_{\text{core}}$ contain nuclear and electronic potential and kinetic energy operators of the $n-1$ electron molecular ion core, $h(\hat{r})$ is the angular operator of the Rydberg electron and

$$h(r) = -(\frac{1}{2})d^2/dr^2 + \ell(\ell + 1)/2r^2 + V_{\text{SCF}} \quad (A3)$$

is the effective one-electron Hamiltonian of the Rydberg electron. Assuming that the nuclei are fixed in their equilibrium positions, and that vibronic coupling can be explicitly excluded, the rotational kinetic energy operator appearing in T_N^+ is given by

$$T_{\text{rot}}^+ = \frac{1}{2} \sum_i \mu_{ii}^e [J_c - p_c - (L + S)_c]_i^2 \quad (A4)$$

where μ_{ii}^e is the equilibrium moment of inertia tensor of the core and J_c , p_c and $(L + S)_c$ are the total, vibrational and electronic (orbital plus spin) angular momentum operators of the freely rotating core referred to a molecule-fixed coordinate system (i.e., $i = x, y, z$). Crossterms between electronic and nuclear motions (e.g., Coriolis and vibronic interactions) are not small in CH_3I and these must be considered explicitly. A similar expression can be written for the kinetic energy operator T_N in the region A description in terms of electronic, vibrational and rotational operators as well. Finally, $T_N \rightarrow T_N^+$ as the electron-ion core distance increases.

The separation of H into $h(r)$ and H_c is exact for infinitely large separations of the fragments. For finite distances, V is given by a sum of electron-electron interaction operators, V_{ee} , and electron-nuclear coupling operators, V_{eN} . The range of these terms serves to define an effective core boundary, r_2 . Thus

$$V_{\text{SCF}} = -1/r; V = 0; \text{ for } r > r_2 \quad (A5)$$

The following terms appear in V :

- The exchange operator between the Rydberg electron and the $(n-1)$ core electrons, V_{ex} ;
- Spin-orbit coupling operators, V_{so} , that are not included in H_c ;
- Spin-spin operators, V_{ss} , that are not included in H_c ;
- The orbital-rotation operator, V_{JL} , which is responsible for ℓ -uncoupling;
- The spin-rotation operator, V_{JS} ; and
- The dynamic vibronic interaction operator, V_{pL} .

The first three terms

$$V_{ee} = V_{\text{ex}} + V_{\text{so}} + V_{\text{ss}} \quad (A6)$$

mix only electronic quantum numbers while the last three,

$$V_{eN} = V_{\text{JL}} + V_{\text{JS}} + V_{\text{pL}} \quad (A7)$$

couple electronic and nuclear motions. Note that Eqn. A7 for a pure s Rydberg state in the absence of degenerate vibrations reduces to

$$V_{eN} \sim V_{\text{JS}} \quad (A8)$$

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16. The designation 6sR refers variously to the 6sa₁ orbital, to the configuration ... 1e⁴a₁²2e³6sa₁, to the states 1-4 derived from this configuration, and to transitions from the ground electronic state to states 1-4.
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21. The quantum number G is defined as follows: the total molecular wavefunction is invariant to operations of the molecular symmetry (MS) group and, in particular, to permutation of equivalent nuclei. In the C_{3v} MS group, permutation can be represented as a rotation about the molecular symmetry axis by a factor 2/3. The resulting rotation (R_z^{2π/3}) then has the effect

$$R_z^{2\pi/3} \psi_{JM} = e^{-2\pi i G/3} \psi_{JM}$$

where G is Hougen's quantum number. The MS group is discussed in detail in Ref. 22.

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