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Rotational autodetachment of FeO$^-$ complexes

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If the neutral molecule core of a molecular negative ion has sufficient rotational energy, the weakly bound electron will autodetach by transfer of molecular rotational energy to this electron. Under certain circumstances, this process can be theoretically described by an analogy with the internal-conversion mechanism of nuclear physics. The internal-conversion mechanism is described and its applicability to the calculation of rotational autodetachment transition rates discussed. It is shown that under the conditions for applicability of the internal-conversion model, this model is equivalent to, but much simpler than, the conventional nonadiabatic couplings (both couplings, not just the gradient-gradient coupling) which result from the breakdown of the Born-Oppenheimer approximation. One state of FeO$^-$, which satisfies the criteria, has a very distinctive dependence of autodetachment transition rate on rotational quantum number. With the help of the internal-conversion model, this dependence is reasonably well described.

I. INTRODUCTION

In a laser spectroscopy investigation of autodetaching resonances in FeO$^-$, Andersen *et al.*[1] observed negative-ion states which they designated as the negative-ion complexes FeO[$^5\Delta_3$]-*s* and FeO[$^5\Delta_3$]-*p*, for which the dependence of the autodetachment rate on rotational quantum number was very different from that of the $A\,^4\Delta_{5/2}$ valence state of FeO$^-$. In their notation, the quantum numbers in square brackets describe the spin-orbit state of the ground-state neutral FeO molecule, which acts as the core of the FeO$^-$, while the loosely bound negative-ion electron moves in an essentially ($l=0$)- or ($l=1$)-type atomic state about that core (hence the appended -*s* and -*p*). An analysis of the experimental data of Andersen *et al.* presented in Sec. III suggests that the FeO core state may not be a pure $^5\Delta$ multiplet, but may exhibit significant spin-orbit coupling. Nevertheless, their nomenclature will be used throughout this work for identification purposes. The [$^5\Delta_3$]-*s* excited state of FeO$^-$ is electronically stable, lying some 35 cm^{-1} below the $^5\Delta_4$ ground state of FeO (see Fig. 1). This binding energy is, however, sufficiently small that there exist rotational states of the molecular core that bring the overall molecular energy for this electronic state above the energies of some lower rotational states of the $^5\Delta_4$ ground state of FeO and also above the $^5\Delta_3$ excited state. These rotational states are unstable against electron detachment by the transfer of molecular rotational energy into electronic energy. Very small detachment rates were found for rotational states in the energy range between the $^5\Delta_4$ ground and $^5\Delta_3$ excited states of FeO, and these rates increase in a roughly linear manner with increasing J. Above the $^5\Delta_3$ energy threshold the autodetachment rates exhibit a dramatic increase with increasing J (see Fig. 2).

Autodetachment of states of the type described by Andersen *et al.* as FeO[$^5\Delta_3$]-*s* and -*p* should be treatable within the formulation of the internal-conversion process of nuclear physics. The requirements for the validity of the internal-conversion formulation are that the loosely bound electron shall in zeroth order be describable by a potential which is independent of the details of the structure of the nucleus. In the nuclear-physics case, this is the potential produced by a point charge Ze. For the case of vibrational autoionization of Rydberg states of H$_2$, Russek, Patterson, and Becker[2] showed that for initial states which satisfied the requirements for its validity, the internal-conversion formulation gave exactly the same re-

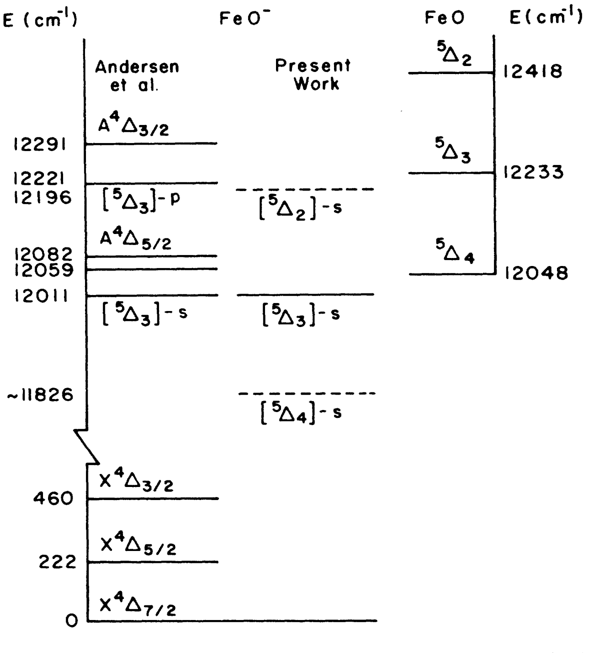

FIG. 1. Energy-level diagram for FeO$^-$ and FeO. On the left, the level scheme of Andersen *et al.* is reproduced. To the right of that, the FeO[$^5\Delta_N$]-*s* scheme used in the interpretation described in the present work is shown. On the extreme right, the ground-state of neutral FeO is also shown.

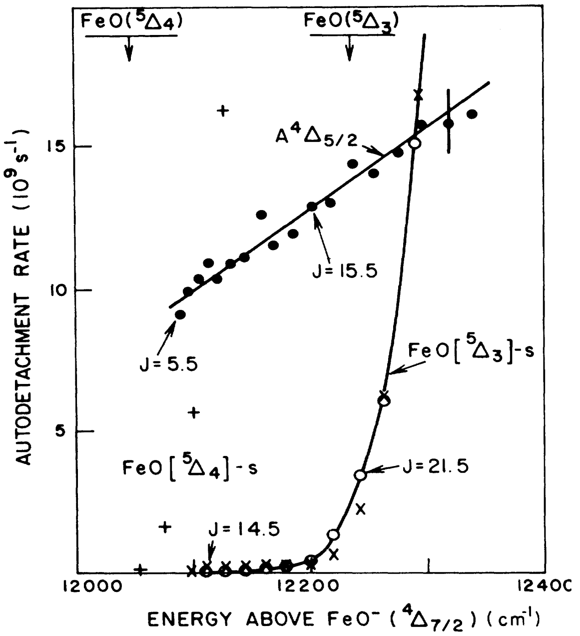

FIG. 2. Autodetachment rates for the valence $A\,^4\Delta_{5/2}$ state, and the FeO[$^5\Delta_3$]-*s* and FeO[$^5\Delta_4$]-*s* states. Only experimental rates, reproduced from Andersen *et al.*, are shown for the valence state, since the internal-conversion model does not treat this state. The rates measured by Andersen *et al.* for the FeO[$^5\Delta_3$]-*s* state are shown as the open circles. The crosses show the calculated values for this state, listed in Table I. Predicted values for the FeO[$^5\Delta_4$]-*s* are shown by +. Andersen *et al.* claim to see autodetachments from this state, but did not report the rates.

sults as the nonadiabatic-coupling formulation of Berry.[3] Although rotational detachment of negative ions may at first sight seem to be an altogether different process from vibrational autoionization of Rydberg states of neutral molecules, the underlying mathematical description of these two processes are quite the same.

What is of interest in the context of the results of Andersen *et al.* is that the states which they describe in terms for which the internal-conversion mechanism ought to be valid exhibit autodetachment rates which are very different from the autodetachment rates exhibited by the valence $A\,^4\Delta_{5/2}$ state, which cannot be treated within the internal-conversion formulation.

The internal-conversion formulation of the autodetachment process is presented in Sec. II, with a proof of the equivalence of this formulation with the usual nonadiabatic coupling deferred to Appendix A. The proof, a generalization of that given in Russek, Patterson, and Becker[2] to encompass rotational autodetachment, is valid only when the following two important conditions are met:

(1) The weakly bound electron makes a negligible contribution to the core structure (i.e., a negligible contribution to the core Hamiltonian).

(2) The dominant contribution of the core to the potential governing the motion of the weakly bound electron must be a term which is independent of the orientation of the core (a monopole or an averaged dipole). The potential terms produced by the core which do depend on the details of core orientation must be sufficiently small as to be treated within the framework of a perturbation expansion.

The internal-conversion formulation does not introduce any new physics. It can be regarded merely as a convenience, which greatly simplifies the calculation of autodetachment transition matrix elements for those initial states for which it is applicable. It does more than just that, however. It also provides a conceptual framework for better understanding the dependences of the autodetachment transition rates on the quantum number N describing the rotational state of the molecular negative ion. This is most important for such a complicated system as FeO$^-$, because different *ab initio* calculations[4,5] are not even able to agree on the ground state of FeO. It would, thus, seem hopeless at this time to attempt an *ab initio* calculation of the autodetachment transition rates. Nevertheless, it will be seen that the J dependence exhibits a characteristic behavior which can be understood with the help of the internal-conversion formulation. The internal-conversion formulation provides simple formulas for the autodetachment rates, with phenomenological parameters that can be adjusted from experimentally obtained information. In the discussion section, Sec. IV, the conceptual framework obtained from the internal-conversion formulation will be translated into the conventional nonadiabatic-coupling terminology.

II. THE INTERNAL-CONVERSION FORMULATION

An excited nucleus can decay either by emitting a γ-ray photon or by internal conversion, a process whereby the excited nucleus transfers its excitation energy directly to an atomic electron (generally a K-shell electron), thereby ejecting it. In the theoretical treatment of internal conversion, the unperturbed Hamiltonian H_0 is the sum of two disjoint terms; one describes the nuclear motion, while the other describes the atomic electron. Only the perturbation term of H couples the two constituents, mediating a transition in which energy is exchanged between the two.

$$H(\mathbf{r},\boldsymbol{\rho})=H_c(\boldsymbol{\rho})+H_e(\mathbf{r})+V(\mathbf{r},\boldsymbol{\rho})=H_0+V(\mathbf{r},\boldsymbol{\rho}) , \tag{1}$$

where $\boldsymbol{\rho}$ stands for the coordinates of all constituents of the nucleus. The eigenfunctions of H_0 are of the form

$$\psi_{N,n}(\mathbf{r},\boldsymbol{\rho})=\Phi_N(\boldsymbol{\rho})\phi_n(\mathbf{r}) \tag{2}$$

and the probability for ejecting the electron is given by

$$w=2\pi\,|M\,|^2\rho(E_k) , \tag{3}$$

where

$$M=\langle\Phi_F(\boldsymbol{\rho})\phi_k(\mathbf{r})\,|\,V(\mathbf{r},\boldsymbol{\rho})\,|\,\Phi_I(\boldsymbol{\rho})\phi_n(\mathbf{r})\rangle . \tag{4}$$

In the context of molecular negative ions, the "nucleus" is the neutral molecule core and the ejection of the loosely bound electron is known as autodetachment. In this case, $H_c(\mathbf{r}_i,\mathbf{R})$ is the Hamiltonian for the neutral molecule core, while

$$H_e=p^2/2m_e+v_0(\mathbf{r}) , \tag{5}$$

where v_0 is some combination of a monopole potential plus a representative dipole potential, $V(\mathbf{r},\mathbf{R}_0)$, generated by the core, and

$$V(\mathbf{r},\mathbf{R})=-Dr(\cos\gamma-\cos\gamma_0)/(r^2+d^2)^{3/2} \tag{6}$$

is the deviation of the instantaneous electron-core interaction potential from the potential included in H_e. The interaction term is here approximated by a dipole-interaction term with dipole moment $\mathbf{D}=qd\hat{R}$, with $\hat{R}$ a unit vector pointing along the inernuclear axis and d a characteristic distance of the order of the size of the molecule. Finally, γ is the angle between $\mathbf{r}$ and $\mathbf{R}$. The essence of the autodetachment process can be succinctly summarized. A dipole potential of sufficient strength will bind an s electron no matter in which direction, $\hat{\mathbf{R}}_0$, that dipole moment points. However, if the direction rotates, then the bound electron rotates with it, producing a centrifugal force. In the molecular analogue to internal conversion, the adiabatic approximation for core motion dictates that the overall state of the negative ion is written as a product of three terms,

$$\psi=\Phi_{CN}(\mathbf{r}_i;\mathbf{R})\chi_{v,J}(\mathbf{R})\phi_n(\mathbf{r}) , \tag{7}$$

where Φ describes the adiabatic electronic state of the core, χ the vibration-rotation state of the core, and ϕ the state of the loosely bound electron. The matrix element, M, is given by

$$M=\langle\psi_F\mid V\mid\psi_I\rangle=\langle\Psi_{CF}\mid\Phi_{CI}\rangle\langle\chi_{J'}\phi_k\mid V\mid\chi_J\phi_n\rangle . \tag{8}$$

In Eq. (8) dependence of the core state on vibrational quantum number v has been supressed, inasmuch as no vibrational excitation is here being discussed. In the adiabatic approximation for the core state, the electronic state of the core will not change in the detachment process, since the interaction term V given by (6) does not involve the core electrons. However, the experimental data indicate that nonadiabatic coupling within the rotating core actually does couple different electronic states to a small, but detectable extent. Hence the factor $\langle\Phi_{CF}\mid\Phi_{CI}\rangle$ is not simplified to $\delta_{CF,CI}$.

A second important property of the matrix element given by (8) together with the electric dipole interaction (6) is the existence of a pseudo-selection-rule. Many of the rotational states with energies just above the detachment threshold can detach only if the core gives up several units of angular momentum. However, since the dipole interaction can change the core by only one unit of angular momentum, these transitions can occur only in higher order. Each additional order beyond the first brings in an additional matrix element and energy denominator. Approximating this ratio by a constant, A, then the ith order contribution, M_i, to the matrix element M is given by

$$M_i=\langle\Phi_{CF}\mid\Phi_{CI}\rangle M_1 A^{J_I-J_F-1} , \tag{9}$$

where $J_F=J_I-i$. Equation (9) is just a rough approximation for the dependence of M_i on the number of rotational quanta needed to eject the electron. It is justified in Appendix C. If $A<1$, then M_i monotonically decreases as the order of the transition increases, albeit not as strongly as in the nuclear internal-conversion process. For the negative-ion detachment process, A^2 is of the order of 0.5, so that several orders will contribute significantly to the detachment rate. For each J_I, there is both a maximum and a minimum value for the possible order i of a transition matrix element. The minimum order n of a transition is the minimum number of units of angular momentum that the core must give up in order to transfer an energy to the loosely bound electron greater than its binding energy E_d. The maximum order possible, denoted by m, is limited by the amount of molecular rotational energy available in the initial state,

$$m=J_I-J_{\text{int}} , \tag{10}$$

where J_{int} is the intrinsic angular momentum of the core. The transition rate is given by Eq. (3), where the matrix element M is given by a perturbation series M_i which must be summed over all orders,

$$M=\sum_{i=n}^{m} M_i . \tag{11}$$

Because different contributions to M_i involve different final states, these contributions add incoherently to $\mid M\mid^2$, giving

$$w=2\pi\sum_{i=n}^{m}\mid\langle\Phi_{CF}\mid\Phi_{CI}\rangle\mid^2\mid M_1\mid^2 A^{2(i-1)}T_i^{1/2} , \tag{12a}$$

where T_i is the kinetic energy of the detached electron when the energy of i units of core angular momentum is transferred to the weakly bound electron,

$$T_i=B[(2J+1)n-n^2]-E_d . \tag{12b}$$

The factor $T_i^{1/2}$ arises from the available phase space for the outgoing electron in the density of final states $\rho(E_i)$ in (3). The remaining factors of $\rho(E_i)$ have been absorbed into $\mid M_1\mid^2$.

III. AUTODETACHMENT IN FeO$^-$

A. Decay of the valence state of FeO$^-$

Figure 1 shows an energy-level diagram for FeO$^-$, with the level scheme of Andersen *et al.* shown on the left, and the FeO[$^5\Delta_N$]-s levels discussed in the present work to the right. The black circles in Fig. 2, reproduced from Andersen *et al.*,[1] show the autodetachment transition rates obtained by them for the $A\ ^4\Delta_{5/2}$ valence state of FeO$^-$, which cannot be treated in the internal-conversion formulation. It can be seen that the rotational state dependence of the decay rates for this state is qualitatively different from that for the FeO[$^5\Delta_N$]-s states in Fig. 2, for which the internal-conversion formulation should be valid.

B. Decay of the FeO[$^5\Delta_N$]-s states of FeO$^-$

Andersen *et al.* hold the neutral FeO core to be a $^5\Delta$ multiplet, showing the $^5\Delta_4$, $^5\Delta_3$, and $^5\Delta_2$ components. In their notation, what appears to the left of the hyphen describes the state of the neutral FeO core, while the quantum designation to the right of the hyphen describes the state of the weakly bound electron. If a very weakly bound *s* electron attaches to this core, a corresponding multiplet of $\mathrm{FeO^-}$ states is expected to exist. The $\mathrm{FeO}[{}^5\Delta_3]$-*s* state is least controversial, and will therefore be considered first. The experimental autodetachment transition rates obtained by Andersen *et al.* are reproduced in Fig. 2. For this state, the major features exhibited by the autodetachment rates as a function of rotational quantum number are the following:

(1) The existence of a small autodetachment rate which increases with rotational quantum number for rotational states between the autodetachment threshold and the ${}^5\Delta_3$ neutral threshold, which occurs at $J=\frac{39}{2}$.

(2) A dramatic but continuous increase in autodetachment rate as a function of rotational quantum number above the $J=\frac{39}{2}$ threshold rotational quantum number, a threshold for which autodetachment to the ${}^5\Delta_3$ state of neutral FeO becomes energetically possible.

Below the $J=\frac{39}{2}$ threshold (i.e., in the energy range between the ${}^5\Delta_4$ and ${}^5\Delta_3$ states of FeO), detachment can only occur if the electronic state of the core changes from ${}^5\Delta_3$ to ${}^5\Delta_4$. Such a transition cannot arise from V, since V does not involve the coordinates of the core electrons. Thus, in the approximation in which the core is treated adiabatically, the transition matrix element vanishes, because the initial and final adiabatic electronic states Φ_{CI} and Φ_{CF} are orthogonal to each other. It must be remembered, however, that adiabatic electronic states are calculated with fixed nuclei. If the core is rotating, a small deviation from adiabatic behavior mixes the two pure ${}^5\Delta_4$ and ${}^5\Delta_3$ electronic states of the FeO core. This nonadiabatic rotational coupling is well known since the early days of molecular physics, and has been used to discuss Λ doubling.[6,7] A more compact treatment of the subject can be found in Landau and Lifshitz.[8] An alternative derivation of the rotational coupling term is presented in Appendix B. This latter derivation is valid when the angular momentum of core rotation $\mathbf{N}$ is large compared with $\Lambda+\Sigma$, so that $\mathbf{J}$ and $\mathbf{N}$ are nearly colinear. In this case, the core angular velocity ω can be taken as approximately constant and approximately equal to $\mathbf{J}/I$, where I is the moment of inertia of the core. When applicable, the derivation given in Appendix B is both simpler to use and more straightforward.

Thus, the proper notation for the two electronic states should be the admixtures Φ_{CL} and Φ_{CM}, where L, M, and U stand for lower, middle, and upper. The mixing is small, so that a perturbative treatment suffices,

$$\Phi_L=\Phi_4+a\Phi_3 \ , \tag{13a}$$

$$\Phi_M=\Phi_3-a\Phi_4 \ , \tag{13b}$$

where the subscripts 3 and 4 denote the adiabatic states which Andersen *et al.* describe as $|{}^5\Delta_3\rangle$ and $|{}^5\Delta_4\rangle$. It will be seen below that the value for M_c predicted by ${}^5\Delta$ states considerably overestimates the value obtained from the data of Andersen *et al.* It is therefore suggested that these states may not be pure Δ states, but an admixture due to coupling of the orbital motion with the spin. In any event, the projections 3 and 4 will be valid quantum numbers, so that the states will be denoted by $|3\rangle$ and $|4\rangle$. Equation (13b) is incomplete, since Φ_3 also mixes with Φ_2 as well as with Φ_4. However, that coupling is not important in the energy range under consideration. The mixing coefficient a is given by

$$a(J)=-2JBM_c/(\varepsilon_3-\varepsilon_4) \ , \tag{14}$$

$$M_c=\langle 4\,|\,L_x+S_x\,|\,3\rangle \ . \tag{15}$$

Since neither L nor S are constants of the motion (only L_z+S_z), the matrix element can only be calculated if exact *ab initio* states are available. Therefore, M_c is here taken as an adjustable parameter. Depending on how the spin couples (or does not couple) to the electronic orbital motion, M_c can range anywhere from zero to a value somewhat larger than unity. To understand this, it will be assumed for heuristic purposes that the core states are predominantly $L=2$, despite the fact that L is not a constant of the motion in a diatomic molecule,

$$\Phi_4=|4\rangle=|L=2,L_z=2,S=2,S_z=2;j=4,j_z=4\rangle \ .$$

The lower case **j** is here used to represent the total angular momentum of electronic motion, since **J** has been reserved for the total angular momentum of the entire molecule, in order to maintain consistency with the notation of Andersen *et al.* The state $|4\rangle$ is both a Hund's-rule state, ${}^5\Delta_4$, and one for which j and j_z are valid quantum numbers. Three different cases will be considered for $\Phi_3=|3\rangle$: Hund's rule (a) and the two couplings of **L** with **S** which give rise to the extreme values of M_c.

Case 1, Hund's rule (a). $|3\rangle=|{}^5\Delta_3\rangle=|L=2, L_z=2,S=2,S_z=1\rangle$. In this case, **L** and **S** are decoupled from one another; each couples only to the nuclear axis, and $\mathbf{j}=\mathbf{L}+\mathbf{S}$ is not a constant of the motion. Inasmuch as the orbital motion is unaltered in the transition, the matrix element of j_x is equal to that for S_x alone,

$$\langle 3\,|\,j_x\,|\,4\rangle=\langle 3\,|\,S_x\,|\,4\rangle=1 \ .$$

It will be seen in the comparison with the experimental data below that this value is much too large, suggesting that these states are not a Δ multiplet.

Case 2, $|3\rangle=|L=2,S=2;j=3,j_z=3\rangle$. For this case and the one which follows, neither L_z nor S_z separately is a constant of the motion. For case 2, $\langle 3\,|\,j_x\,|\,4\rangle=0$; since j_x acting on $|4\rangle$ does not change the value of j, the matrix element between a $j=3$ state and a $j=4$ state vanishes. Thus it is seen that M_c can be as small as zero.

Case 3, $|3\rangle=|L=2,S=2;j=4,j_z=3\rangle$. For this case, $\langle 3\,|\,j_x\,|\,4\rangle=2^{1/2}$.

For the $|3\rangle$ and $|4\rangle$ states of FeO, with B and $\varepsilon_3-\varepsilon_4$ taken from Andersen *et al.*,

$$a(J)=-0.0056JM_c \ . \tag{16}$$

It will be noted in Eqs. (13) that for fixed J, Φ_L and Φ_M are orthogonal, but that the overlap does not vanish if the two are computed for different J,

$$\langle\Phi_{CF}\,|\,\Phi_{CI}\rangle=\langle\Phi_L\,|\,\Phi_M\rangle=-0.0056(J_I-J_F)M_c \ . \tag{17}$$

The detachment energy for the $\mathrm{FeO}[{}^5\Delta_3]$-*s* state to the ${}^5\Delta_4$ state of neutral FeO is given by Andersen *et al.* as

$E_d = 35$ cm^{-1}, although there is some uncertainty about that value. With the rotational constant $B = 0.517$ cm^{-1} for the $^5\Delta$ states, the lowest rotational level above the detachment limit is the $J = \frac{17}{2}$ state, with $E_J = 41$ cm^{-1}. However, this state can detach only in sixth or higher order. The minimum orders of the transitions for the detachable states below the FeO $^5\Delta_3$ energy threshold are listed in Table I, where E_d has been taken to be 37.2 cm^{-1}. This value is well within the experimental uncertainty for E_d, and makes the interpretation more reasonable.

For detachment to the $^5\Delta_N$ state of neutral FeO, the contribution of order i to the transition rate below the ε_N threshold is given by

$$w_i = CR^2M_c^2(A^2)^{i-1}T_i^{1/2}\ , \tag{18a}$$

$$R = -2B/(\varepsilon_N - \varepsilon_{N-1})\ ,$$

while the detachment rate for a transition of ith order to the $^5\Delta_N$ state of neutral FeO above the ε_N threshold is given by

$$w_i = C(A^2)^{i-1}T_i^{1/2}\ . \tag{18b}$$

The factor C incorporates the 2π in Eq. (3) as well as all the factors of $\rho(E_i)$ except $T_i^{1/2}$ (in cm$^{-1/2}$), where T_i is the kinetic energy of the detached electron. In addition, it contains a normalization adjustment, since the matrix element M_1 is not calculated.

For the FeO[$^5\Delta_3$]-s state, $N = 3$. The values for the parameters found for best fit with the experimental transition rates are $C = 5800$, $M_c^2 = 0.034$ and $A^2 = 0.5$. The value for R is not adjusted, but is obtained from the value for B and the energy difference adopted by Andersen *et al.*: $R = 0.0056$. With these adopted values, Table I lists for all rotational levels the separate detachment rates for the FeO[$^5\Delta_3$]-s state of FeO$^-$ to the $^5\Delta_4$ and to the $^5\Delta_3$ states of FeO. Table I also lists the total transition rates, which is the sum of the two, and compares the theoretical detachment rates with those measured by Andersen *et al.* Because the adjusted value for M_c imposed by the experimental data turns out to be so much smaller than that predicted by the Hund's rule (a) state (0.18, as compared with 1.0), the Hund's rule description may not be valid. The interpretation of the experimental data here presented suggests that **L** and **S** strongly couple, and that L_z (i.e., Δ) is not a good quantum number describing the state.

From the model of an s electron loosely bound to a neutral FeO core in one of the components of the $^5\Delta_N$ multiplet, it follows that there should exist a corresponding multiplet of FeO$^-$: FeO[$^5\Delta_N$]-s. Since the loosely bound electron is, to a first approximation, independent of the details of core structure, the separation between these states of the molecular negative ion should be 185 cm^{-1},

TABLE I. Autodetachment transition rates for the FeO[$^5\Delta_3$]-s state. The transition rates for transitions to the $^5\Delta_4$ state have been calculated from Eq. (18a), while transitions to the $^5\Delta_3$ have been calculated from Eq. (18b). The constant C has been taken to be 5800, with $M_c^2 = 0.034$ and $A^2 = 0.5$. No listing indicates no transition is possible. No experimental results were given by Andersen *et al.* for $J > \frac{47}{2}$, because the peaks were too broad to be analyzed.

	Transitions to $^5\Delta_4$ state of FeO			Transitions to $^5\Delta_3$ state of FeO			Total transition rates (10^9)	
J	n	m	$\sum_i w_i$	n	m	$\sum_i w_i$	Theory	Experiment
$\frac{17}{2}$	6	6	0.00				0.00	not observed
$\frac{19}{2}$	5	7	0.04				0.04	not observed
$\frac{21}{2}$	4	8	0.08				0.08	not observed
$\frac{23}{2}$	4	9	0.14				0.14	not observed
$\frac{25}{2}$	4	10	0.17				0.17	not observed
$\frac{27}{2}$	3	11	0.22				0.22	>0
$\frac{29}{2}$	3	12	0.26				0.26	0.07
$\frac{31}{2}$	3	13	0.29				0.29	0.11
$\frac{33}{2}$	3	14	0.32				0.32	0.15
$\frac{35}{2}$	3	15	0.34				0.34	0.19
$\frac{37}{2}$	2	16	0.37				0.37	0.28
$\frac{39}{2}$	2	17	0.40				0.40	0.40
$\frac{41}{2}$	2	18	0.43	18	18	0.05	0.48	1.31
$\frac{43}{2}$	2	19	0.46	15	19	1.77	2.23	3.47
$\frac{45}{2}$	2	20	0.48	14	20	5.59	6.07	6.02
$\frac{47}{2}$	2	21	0.50	12	21	16.09	16.59	15.10
$\frac{49}{2}$	2	22	0.52	12	22	27.44	27.96	

the same as the known separation between components of the $^5\Delta$ triplet of neutral FeO. That would predict the FeO[$^5\Delta_2$]-*s* state of FeO$^-$ to be at $\sim 12\,196$ cm^{-1}, and the FeO[$^5\Delta_4$]-*s* to be at $\sim 11\,826$ cm^{-1}.

Andersen *et al.* did indeed find what appears to be two close-lying states at $\sim 12\,221$ cm^{-1}, reasonably close to the predicted value of $\sim 12\,196$ cm^{-1}, for which the dependences of the autodetachment transition rate on rotational quantum number J are quite similar to that found for the FeO[$^5\Delta_3$]-*s* state. However, the thresholds at which the autodetachment rates begin to rise steeply with increasing J are located at $\sim 12\,283$ cm^{-1} and $\sim 12\,375$ cm^{-1}, neither of which corresponds to any state of the $^5\Delta_N$ triplet of neutral FeO. Andersen *et al.* interpret these states as a doublet of FeO[$^5\Delta_3$]-*p* states. Such an identification would indeed account for a doublet, but does not account for the puzzling threshold energies. A possibility that could account for both the doublet character and the threshold energies is a nonadiabatic rotational coupling between the $A\,^4\Delta_{3/2}$ and FeO[$^5\Delta_2$]-*s* states of FeO$^-$. However, because of the uncertainty surrounding these states, they will not be analyzed in this work. Further work on these states must await a more complete experimental description.

The third state of the FeO$^-$ triplet is the FeO[$^5\Delta_4$]-*s* state. Andersen *et al.* found some transition lines in their spectra which they attributed to this state, but they were not sufficiently confident to list any transition rates for this state. The plus symbols in Fig. 2 show the rates calculated in this work for that state. Since there is no lower state of the FeO core to mix, only the contributions to the transition rate given by Eq. (18b) are applicable. As a consequence, only a few rotational states in the sharply rising J dependence are predicted to fall within the limits they are able to measure.

IV. DISCUSSION

As stated in the Introduction, the internal-conversion formulation does not introduce any new physics. Rather, it is a tool which simplifies the calculation of rotational autodetachment transition matrix elements for the initial states for which it is applicable. It provides a simple formula for the transition rates with two phenomenological parameters, which can be adjusted from experimentally obtained information. In addition, a nonadiabatic mixing of adiabatic electronic states of the core, due to its rotational motion, has been introduced to account for the sudden change in the J dependence of the autodetachment rates at the $^5\Delta_N$ thresholds. Here too, the internal-conversion formulation provides a simple formula, with the introduction of a third parameter. With the parameters adjusted, the fit of the theory to the experimental detachment rates for the FeO[$^5\Delta_3$]-*s* state of FeO$^-$ investigated by Andersen *et al.* is rather good. Additionally, the detachment rates for the FeO[$^5\Delta_4$]-*s* state are predicted. This state was seen, but not investigated, by Andersen *et al.*

The successive "orders" of the transition rates refer to the number of quanta of core rotational angular momentum lost by the core, the energies of which are transferred to the detached electron. There are but a finite number of orders, determined by the minimum amount of rotational energy needed to detach the electron for one limit, and for the other limit, the total available amount of core rotational energy. If one elects not to introduce the internal-conversion formulation, but to stick with conventional nonadiabatic coupling, then the orders w_i of transitions simply become the different final rotational states of the residual FeO neutral molecule after detachment. If, as one would suspect, not all final rotation states are equally probable, but that the probabilities successively decrease as $J_I - J_F$ increases, then a parameter A^2 would have to be introduced to quantify how much. The second parameter is, of course, the size of the largest rate. The near linear dependence of the small transition rates below the core threshold has already been described in terms of nonadiabatic coupling even in the internal-conversion conceptual framework. This behavior requires a third and final parameter to describe the rigidity of the core adiabatic states against nonadiabatic rotational mixing.

Finally, a few words on why the internal conversion mechanism is inappropriate to study the detachment rates of the $A\,^4\Delta_N$ valence states. The internal-conversion formulation requires that to lowest order, the core and the weakly bound electron are uncoupled. Thus, the interaction term V must be insignificant in forming the states of H_0; it merely mediates the transition between initial and final states of H_0. This is not true for the $A\,^4\Delta_N$ states. Here, V is important in determining the initial state as well as in mediating the transition. In this case, V must be decomposed by means of projection operators P and Q into $PVP+QVQ$, which is incorporated into H_0 and determines the states, plus the terms $PVQ+QVP$, which mediate the autodetachment transitions. (Indeed, this is precisely what must be done in describing autoionization of doubly excited states of atoms.)[9] A semiphenomenological treatment of the valence states would have to take into account the fact that the initial state already has a substantial overlap with the $^5\Delta_N$ core state, so that all detachment rates will be substantial. The linear rise in the detachment rates with increasing J merely reflects the increasing number of final states with increasing J_I.

Note added in proof. In the work of T. Andersen *et al.*, Ref. 1(b), the nomenclature for the FeO[$^5\Delta_3$]$-s$ state of FeO$^-$ has been changed to $B\,^4\Delta_{7/2}$, in keeping with more customary spectroscopic notation.

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APPENDIX A

In this appendix the approximate equivalence of the internal-conversion formulation with the nonadiabatic coupling formulation will be established. It will be shown that the transition matrix element M_{IC} obtained from the internal-conversion formulation, is mathematically equal to M_{NAC}, the transition matrix element which follows from the nonadiabatic-coupling formulation, provided that a condition is fulfilled which is approximately realized when a diffuse electron interacts with a small, massive core.

Let $\chi_i(\mathbf{R})$ and $\chi_f(\mathbf{R})$ be vibrational-rotational eigenfunctions of the Hamiltonian describing the motion of the nuclei,

$$[-(1/2M)\nabla_R^2+V_c+v(\mathbf{R})]\chi_n=E_n\chi_n \ . \tag{A1}$$

Here M stands for the reduced mass, V_c for the contribution to the adiabatic potential due to the core constituents, and $v(\mathbf{R})$ for the electronic contribution of the loosely bound electron to the potential energy. The exact equality of the internal-conversion matrix element and the nonadiabatic coupling matrix element for the transition will be proven, provided that

$$v(\mathbf{R})=v_{fi}(\mathbf{R})=(\Phi_f(\mathbf{r}_j,\mathbf{r};\mathbf{R}) \mid V(\mathbf{r},\mathbf{R}) \mid \Phi_i(\mathbf{r}_j,\mathbf{r};\mathbf{R}) \mid \ , \tag{A2}$$

instead of one of the diagonal terms, $v_{ii}(\mathbf{R})$ or $v_{ff}(\mathbf{R})$. Here, the inner product notation $(|)$ denotes integration only over the electronic coordinates $\mathbf{r}_j$ of the core electrons and $\mathbf{r}$ of the loosely bound electron, and $V(\mathbf{r},\mathbf{R})$ is the interaction term in the full Hamiltonian that couples the loosely bound electron to the core constituents. Of course, the condition (A2) cannot be exactly fulfilled. No potential experienced by a physical system in state i can anticipate the transition to state f. Thus, the equivalence hinges on the approximate condition that v_{ii} and v_{ff} have such a small effect in determining χ_i and χ_f that each may be neglected. In that case each may be replaced by the equally negligible v_{fi}. This condition is approximately satisfied if the loosely bound electron makes a negligible contribution to the nuclear motion (i.e., if for all practical purposes V_c alone determines the core motion).

For convenience, we define a quantity I, given by

$$I=(E_i-E_f)M_{\mathrm{IC}}=(E_i-E_f)\langle \Phi_f\chi_f \mid V \mid \Phi_i\chi_i\rangle \ . \tag{A3}$$

Carrying out the inner product over electronic coordinates yields

$$I=(E_i-E_f)\langle \chi_f(\mathbf{R}) \mid v(\mathbf{R}) \mid \chi_i(\mathbf{R})\rangle \ , \tag{A4}$$

where the brackets $\langle \mid \rangle$ now indicate integration only over $\mathbf{R}$. We can rewrite (A4) using the Schrödinger equations for χ_n,

$$\begin{aligned} I&=\langle \chi_f \mid v \mid [-(2M)^{-1}\nabla_R^2+V_c+v]\chi_i\rangle \\ &\quad -\langle [-(2M)^{-1}\nabla_R^2+V_c+v]\chi_f \mid v \mid \chi_i\rangle \\ &=-(2M)^{-1}[\langle \chi_f \mid v \mid \nabla_R^2\chi_i\rangle-\langle \nabla_R^2\chi_f \mid v \mid \chi_i\rangle] \\ &=-(2M)^{-1}\langle \chi_f \mid [v,\nabla_R^2] \mid \chi_i\rangle \ , \end{aligned}$$

where $[v,\nabla_R^2]$ denotes the commutator. This last step is justified because ∇_R^2 is Hermitean. Expanding the commutator, I can be written in the form

$$I=+(2M)^{-1}\langle \chi_f \mid \nabla_R v)\cdot\nabla_R+(\nabla_r^2 v) \mid \chi_i\rangle \ . \tag{A5}$$

Finally, equating the two expressions for I from Eqs. (A3) and (A5) yields

$$\begin{aligned} M_{\mathrm{IC}}&=\langle \Phi_f\chi_f \mid V \mid \Phi_i\chi_i\rangle \\ &=I/(E_i-E_f) \\ &=[2M(E_i-E_f)]^{-1}[\langle \chi_f \mid 2(\nabla_R v)\cdot\nabla_R\chi_i\rangle \\ &\qquad +\langle \chi_f \mid (\nabla_R^2 v) \mid \chi_i\rangle] \ . \end{aligned} \tag{A6}$$

The matrix element M_{IC} is the transition matrix element which follows from the internal-conversion (IC) formulation. This will be compared with the matrix element M_{NAC} for the transition which follows from the nonadiabatic coupling (NAC) formulation:

$$M_{\mathrm{NAC}}=-(2M)^{-1}\langle \Phi_f\chi_f \mid 2\nabla_R\Phi_i\cdot\nabla_R\chi_i+(\nabla_R^2\Phi_i)\chi_i\rangle \ , \tag{A7}$$

where, to first order, the electronic state is given by

$$\Phi_n=\phi_c(\mathbf{r};\mathbf{R})\left[\phi_n+\sum_j \phi_j V_{jn}/(\varepsilon_n-\varepsilon_j)\right] \ . \tag{A8}$$

Here, $\phi_c(\mathbf{r};\mathbf{R})$ denotes the full adiabatic electronic wave function describing the neutral FeO core, the ϕ_n describe the zeroth-order wave functions for the loosely bound electron in a core potential which is a monopole or averaged dipole (both of which are independent of $\mathbf{R}$), and

$$V_{jn}=\langle \phi_c\phi_j \mid V \mid \phi_c\phi_n\rangle=v_{jn}(\mathbf{R}) \ . \tag{A9}$$

In this treatment, the neutral FeO core is described by an adiabatic wave function, while the weakly bound electron is described only to first order in a perturbation expansion.

Equation (A8) and (A9) are now substituted into the expression for M_{NAC} given by Eq. (A7), remembering that in the expressions for the electronic states, only ϕ_c and v_{jn} depend on $\mathbf{R}$. After some simplification, we obtain, in a first-order perturbative treatment of the loosely bound electron (i.e., to terms linear in v_{mn})

$$\begin{aligned} M_{\mathrm{NAC}}&=-(2M)^{-1}[\langle \chi_f \mid 2\nabla_R v\cdot\nabla_R\chi_i\rangle \\ &\qquad +\langle \chi_f \mid \nabla_R^2 v \mid \chi_i\rangle]/(\varepsilon_i-\varepsilon_f) \ . \end{aligned} \tag{A10}$$

In Eq. (A10), $v(\mathbf{R})$ stands for $v_{fi}(\mathbf{R})$, as defined in (A2). In deriving (A10), we have used the following: $(\phi_m \mid \phi_n)=\delta_{mn}$, $(\phi_c \mid \phi_c)=1$, and $(\phi_c \mid \nabla_R\phi_c)=0$. The zeroth-order term vanished identically, as did the first-order term that contained $(\phi_c \mid \nabla_R\phi_c)$. Two pairs of first-order terms canceled each other, because they were identical except for the energy denominators, which were negatives of one another. We now note that because total energy (nuclear plus electronic) is conserved, $\varepsilon_i-\varepsilon_f$, the energy difference between the initial and final states of the loosely bound electron, is equal to the negative of the corresponding difference in nuclear energies, $-(E_i-E_f)$,

$$\varepsilon_i-\varepsilon_f=-(E_i-E_f) \ . \tag{A11}$$

With Eq. (A11) substituted into Eq. (A10), this latter becomes identical to the expression (A6) for M_{IC}. Thus, we have proven that

$$M_{\mathrm{IC}}=M_{\mathrm{NAC}}\ . \tag{A12}$$

It is important to note that the proof given above is not valid in general. Its validity is dependent on two critical assumptions, which are justified only when the active electron is strongly coupled to the core by a potential which is independent of **R**. Aside from this potential, the residual coupling to the core must be weak. In that case, $v_{ii}=v_{ff}=v_{\mathrm{if}}$, since all three can be approximated by zero. At the same time, the states of the active electron will be essentially determined by a potential which is independent of **R**, with the small residual coupling that *is* dependent on **R** producing only perturbative corrections.

APPENDIX B

The solutions for the adiabatic electronic states of a molecule are always carried out in terms of body-fixed coordinates. Accordingly, this appendix presents a derivation of the molecular Hamiltonian in terms of the rotating body-fixed coordinate system. It must be made clear at the outset that in the derivation which follows, there is *no such thing as a "body-fixed reference frame."* The entire physics is (as it must be) carried out in a space-fixed Newtonian reference frame; the results are merely expressed in terms of the rotating body-fixed coordinates for convenience in calculating the electronic states, since these are always calculated in terms of body-fixed coordinates.

The standard procedure for obtaining the quantum-mechanical Hamiltonian in any coordinate system $q_1,q_2,\ldots,q_N$ requires first finding the Lagrangian in classical dynamics in terms of the classical variables, q_i, and the velocities, $\dot{q}_i$,

$$L=T-V\ . \tag{B1}$$

The kinetic energy must be referred to a Newtonian reference frame. The Hamiltonian of classical mechanics is then given by[10]

$$H=\sum_{i=1}^{N}p_i\dot{q}_i-L\ , \tag{B2}$$

where the momenta p_i are defined to be

$$p_i=\partial L/\partial\dot{q}_i\ . \tag{B3}$$

In the Hamiltonian formulation, the coordinates and momenta are considered to be a set of $2N$ independent variables which fully determine the dynamical system. Therefore, the N velocities must be expressed in terms of the coordinates and momenta from the N equations (B3), and these expressions then substituted into (B2) to make the Hamiltonian a function of q_i,p_i only. All of this is strictly classical physics. The passage to quantum mechanics is accomplished by replacing the N pairs of canonical classical variables q_i,p_i by operators which satisfy the cummutation rules

$$[q_i,p_j]=i\hbar\delta_{ij}\ . \tag{B4}$$

To avoid cumbersome notation, the operators are denoted by the same symbols used for the classical variables. There will be no confusion, because the classical variables are not used once the derivation in this appendix is completed.

Let x', y', z' denote the *space*-fixed coordinate system in the Newtonian reference frame, and let x, y, z denote the body-fixed coordinate system rotating about the common x' and x axes. This choice is unconventional in discussing a rotating coordinate system. The selection was made because all molecular calculations of adiabatic electronic states always use the body-fixed coordinate system and always denote the coordinates simply by x, y, z, with the z direction taken to be along the internuclear axis. The axis of molecular rotation is here taken to be the x axis, and for simplicity the x' axis of the space-fixed system is also taken to lie along this rotation axis. With these choices, the transformation from space-fixed to body-fixed coordinates is given by

$$\begin{aligned} x'&=x\ ,\\ y'&=y\cos(\omega t)-z\sin(\omega t)\ ,\\ z'&=y\sin(\omega t)+z\cos(\omega t)\ . \end{aligned} \tag{B5}$$

For the classical-dynamics problem, the classical variables $\mathbf{r}'(t)$ and $\mathbf{r}(t)$ describe the trajectory of the electron in the respective coordinate systems.

Inasmuch as Newtonian physics (including the Lagrangian formulation thereof) is valid only in a Newtonian reference frame, the kinetic energy of the electron must be referred to a space-fixed coordinate system. Thus,

$$T=(m/2)[(\dot{x}')^2+(\dot{y}')^2+(\dot{x}')^2]\ . \tag{B6}$$

Differentiating the three transformation equations (B5) with respect to time and substituting the result into (B6) yields

$$\begin{aligned} T=&(m/2)(\dot{x}^2+\dot{y}^2+\dot{z}^2)+(m/2)(y^2+z^2)\omega^2\\ &+m\omega(y\dot{z}-z\dot{y})\ . \end{aligned} \tag{B7}$$

The first term gives the kinetic energy relative to the rotating coordinate system. The second term is the so-called "centrifugal potential," which gives rise to the "centrifugal force" that would be experienced by an observer in the body-fixed *frame*. This term can be understood by recognizing that even if the electron is stationary with respect to the molecular axes, it still has a velocity $r\omega$ in the space-fixed frame. The third term gives the Coriolis interaction.

Since the potential V is a function of spatial coordinates only,

$$\partial L/\partial\dot{x}=\partial T/\partial\dot{x}\ ,$$

etc.; thus, L can be replaced by T in Eqs. (B3). The momenta are found to be

$$\begin{aligned} p_x&=\partial L/\partial\dot{x}=\partial T/\partial\dot{x}=m\dot{x}\ ,\\ p_y&=m\dot{y}-m\omega z\ ,\\ p_z&=m\dot{z}+m\omega y\ . \end{aligned} \tag{B8}$$

It is important to note that the momenta in the body-fixed coordinate system are not simply $m\mathbf{v}$, but contain additional terms the significance of which will be discussed below. With the equations (B8) the Hamiltonian can be expressed in terms of **r** and **p**. The algebra is a bit complicated, but quite straightforward,

$$H=(1/2m)(p_x^2+p_y^2+p_z^2)-\omega L_x+V(\mathbf{r}) ,$$

which can be written more compactly as

$$H=H_0-\omega L_x , \tag{B9}$$

where

$$H_0=p^2/2m+V(\mathbf{r}) , \tag{B10a}$$

$$\mathbf{L}=\mathbf{r}\times\mathbf{p} . \tag{B10b}$$

Here, H_0 denotes the Hamiltonian that one would write down for a nonrotating molecule. It is the Hamiltonian the eigenstates of which are the customary adiabatic states (in the adiabatic approximation, of course). The extra term $-\omega L_x$ is treated as a perturbation in this work, since molecular rotational velocities are small. It couples different adiabatic states and is, therefore, a nonadiabatic coupling term. Since all terms in nonrelativistic Hamiltonians are scalars, the perturbation can be more generally expressed as $-\boldsymbol{\omega}\cdot\mathbf{L}$,

$$H=H_0-\boldsymbol{\omega}\cdot\mathbf{L} . \tag{B11}$$

Writing out L_x,

$$L_x=yp_z-zp_y=(ym\dot{z}-zm\dot{y})+m(y^2+z^2)\omega , \tag{B12}$$

where y^2+z^2 is the square of the distance to the axis of rotation. It is seen that L_x is the x component of angular momentum referred to the *space-fixed* frame, a result which is not surprising, since the physics has all been executed in a space-fixed reference frame. The term $mr^2\omega$ in L_x gives the angular momentum the electron would have in the space-fixed frame if it were stationary with respect to the molecular axes.

The interaction term $-\omega L_x$ in H couples states of different z component of *orbital* angular momentum (i.e., Σ to Π). However, all the states under consideration are Δ, but with different z components of spin angular momentum. To generalize the result (B9) to encompass mixing of spin states, one need only recognize that **L** is the generator for infinitesimal rotations in the Hilbert space which describes electron translational motion. In the Hilbert space which describes both spin and orbital coordinates, the corresponding infinitesimal rotation generator is $\mathbf{L}+\mathbf{S}$, giving rise to the nonadiabatic coupling term $-\omega(L_x+S_x)$, or, more generally, $-\boldsymbol{\omega}\cdot(\mathbf{L}+\mathbf{S})$, giving

$$H=H_0-\boldsymbol{\omega}\cdot(\mathbf{L}+\mathbf{S}) . \tag{B13}$$

APPENDIX C

In this appendix, the approximation given by Eq. (9) for the ith-order matrix element M_i will be justified. It is needed when the molecular core must lose more than one unit of rotational angular momentum in order to supply enough energy to the electron to overcome its binding energy. Because the interaction term (6) can change the core angular momentum by only one unit, a change of i units requires calculation of the transition matrix element to ith order.

The starting point is the equation from Schiff[11] relating successive orders i in the amplitude a_k of the kth state in time-dependent perturbation theory,

$$\dot{a}_k^{(i+1)}=-\sum_n H'_{kn}a_n^{(i)}e^{i\omega_{kn}t} , \tag{C1}$$

with

$$\begin{aligned} &a_k^{(0)}=0 \ \text{ for } k\neq I , \\ &a_I^{(0)}=1 . \end{aligned} \tag{C2}$$

Since the matrix elements do not depend on time, Eq. (C1) can be integrated to obtain the first-order term

$$a_k^{(1)}(t)=H'_{kI}(1-e^{i\omega_{kI}t})/\omega_{kI} , \tag{C3}$$

where the kth state must be one for which $N_k=N_I-1$. The only significant contribution to the transition rate will come from a final state F for which energy is conserved,

$$E_F-E_I=\omega_{FI}=0 , \tag{C4}$$

so that

$$a_F^{(1)}(t)=H'_{FI}[(1-e^{i\omega_{FI}t})/\omega_{FI}] . \tag{C5}$$

The transition rate is given by

$$w=2\pi\rho\,|M\,|^2 , \tag{C6}$$

where M is that which multiplies the factor in the square brackets, H'_{FI} in this case.

When two rotational quanta are needed for sufficient energy to eject the electron, then the first-order term cannot conserve energy. It is then necessary to substitute the first-order amplitude (C3) into (C1) and integrate once again,

$$\begin{aligned} a_F^{(2)}(t)=\sum_k &(H'_{Fk}H'_{kI}/\omega_{kI}) \\ &\times[(1-e^{i\omega_{Fk}t})/\omega_{Fk}-(1-e^{i\omega_{FI}t})/\omega_{FI}] . \end{aligned} \tag{C7}$$

Again, by energy conservation, $\omega_{FI}=0$. The first term in the square brackets of (C7) cannot contribute, because neither ω_{Fk} nor ω_{kI} can ever be equal to zero. Moreover, there is only one intermediate state in the sum over k: the one for which the electron is ejected and the core rotational motion has decreased by a single rotational quantum. Thus

$$a_F^{(2)}(t)=-(H'_{Fk}H'_{kI}/\omega_{kI})[(1-e^{i\omega_{FI}t})/\omega_{FI}] . \tag{C8}$$

Assuming all matrix elements are approximately equal, and denoted simply by H',

$$M_2 = M_1 \,|\, -H'/\omega_{kI} \,|^2 = M_1 A^2 \,. \tag{C9}$$

Similarly, when three rotational quanta are needed to eject the electron,

$$M_3 = M_1 \,|\, (H'/\omega_{kI})(H'/\omega_{nI}) \,|^2 = M_1 A^4 \,, \tag{C10}$$

where ω_{nI} is the energy defect when two rotational quanta have been supplied out of the three needed. The energy denominators form a decreasing sequence, but that is ignored in the rough approximation given by Eq. (9) of Sec. II.

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