Vibrationally induced photodetachment of electrons from negative molecular ions

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An analytical theory is described for the vibrationally induced photodetachment of electrons from negative molecular ions with large dipole moments. The approach is based on the use of rotationally adiabatic potential curves which are obtained by diagonalizing a simple charge-dipole interaction potential. The mechanism of the vibrationally induced electron detachment is related to the crossing of an attractive rotationally adiabatic potential-energy curve for the vibrationally excited state with repulsive curves for the vibrational ground state of the parent molecule. A simple Franck-Condon theory is used to treat the curve crossing, and a formula for the linewidths in the photodetachment spectra is derived. An interesting prediction is that, for large values of the total angular momentum J, the linewidths decrease with increasing J. This finding is in agreement with recent experimental results for the photodetachment of electrons in PtN^-.

I. INTRODUCTION

There have been many measurements of high-resolution spectra on negative ions in recent years. One method that has produced particularly detailed spectra is autodetachment spectroscopy.[1,2] This technique normally involves detection of electrons that are photodetached from negative molecular ions in a fast ion beam. When combined with a suitable laser source that can be tuned to frequencies just above threshold for detachment of the electron, this method can yield rotational structure in the photodetachment spectra with sub-Doppler linewidths.[3] Applications to systems with large dipole moments have produced particularly well-resolved spectra.[3-6] Good examples are the measurements of spectra for CH_2CN^- and CH_2CHO^-, which have revealed subtle dependencies of the linewidths on the total angular momentum quantum number J and symmetric top projection quantum number K.[5,6]

We have developed a simple quantum-mechanical theory for explaining this rotational structure in the near-threshold photodetachment spectra for negative molecular ions with large dipole moments.[7] The theory, which has also been applied extensively to the study of ion-molecule reaction rates,[8] involves the calculation of rotationally adiabatic potential curves by diagonalizing a Hamiltonian containing a simple potential constructed from the long-range electron-dipole interaction. For a symmetric top molecule, there is only one attractive rotationally adiabatic potential curve for each J and K. Evaluation of the energies and widths of the shape and Feshbach resonances for these effective potentials are identified with the positions and widths of the lines in the photodetachment spectra. The theory explains several experimental results observed[5,6] for CH_2CN^- and CH_2CHO^-. This includes the regular spacings of the rotational lines, the independence of the linewidths on K for CH_2CN^-, the sharp increase in linewidths with increasing K for CH_2CHO^-, and the effects of isotopic sub-

stitution on the photodetachment spectra.[7] Indeed, the theory predicted[7] that the linewidths for CD_2CDO^- would be roughly one-third those obtained for CH_2CHO^- for the same J and K, and this prediction has been subsequently verified in experiments.[9]

In our previous applications of the rotationally adiabatic theory to photodetachment, the parent molecule was assumed to be in its vibrational ground state for the duration of the photodetachment process.[7] Here we extend the theory to treat the case when the negative ion can be vibrationally excited either before or during the autodetachment process while the parent neutral molecule is produced finally in its ground vibrational state $v = 0$. For a diatomic negative ion AB^-, this process can be pictured as

$$AB^- \xrightarrow{h\nu} AB^-(v=1)^* \longrightarrow AB(v=0)+e^-$$
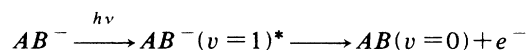
where $AB^-(v=1)^*$ refers to an electronically and vibrationally excited state of AB^- with enough energy to detach the electron to produce $AB(v=0)$ in its ground electronic and vibrational state. Thus the process involves simultaneous vibrational relaxation and electron detachment. This vibrational process is of interest because it has been addressed by some of the photodetachment experiments.[6,9] In the experiments on CH_2CN^-, for example, it was observed[6] that only broad lines without rotational structure could be seen in regions of the photodetachment spectrum where CH_2CN^- would be expected to be vibrationally excited. Furthermore, and more interesting, measurements[10] of photodetachment spectra in the 14 500-to-17 300-cm^{-1} region, using isotopically substituted Pt, showed that the photodetachment of PtN^- involved the vibrational relaxation route

$$PtN^- \xrightarrow{h\nu} PtN^-(v=1)^* \longrightarrow PtN(v=0)+e^- \ .$$
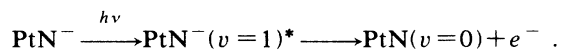
In this case, the linewidths could be measured for J greater than 44, with an unusual decrease in linewidth being observed as J increased.

The somewhat novel feature of the theory that we are proposing is that the rotational structures in the photodetachment spectra are related to potential-energy terms in the electron-molecule Hamiltonian. There is much literature on vibrationally induced autoionization of neutral molecules in which vibrational kinetic energy is assumed to play the major role in ejecting the electron.[11,12] This mechanism has also been used in a very recent paper on vibrationally induced photodetachment of negative molecular ions in which non-Born-Oppenheimer kinetic couplings were calculated.[13] However, for some molecules, the dipole moment and derivative of the dipole moment with respect to the vibrational coordinate will be large, and then the electron-dipole potential-energy terms cannot be ignored. These terms also couple the rotational states of the molecule together and it will often be essential to include them in theories that attempt to explain rotational structures in photodetachment linewidths.[7]

The theory that we are applying to the photodetachment problem is adapted from the type of theory that is commonly used to explain the dissociation of atoms from weakly bound molecular complexes.[14] Here, vibrational energy in the complex can be sufficient to induce dissociation and the process is then called vibrational predissociation as vibrational relaxation is needed to produce the energy for dissociation. Although the terminology is different, this process is analogous to the vibrationally induced detachment of electrons. This is particularly true for the near-threshold detachment of electrons from dipolar molecular negative ions as the electron is then in a very diffuse orbital and, to a good approximation, can be considered as an independent particle. Thus there are important analogies between weakly bound electron-molecule and atom-molecule complexes that should be realized. Indeed, the rotational structures in the spectra for vibrational predissociation of van der Waals complexes[14] can look very similar to those observed in the spectra for vibrationally induced photodetachment.[10]

In Sec. II we describe the rotationally adiabatic theory. In Sec. III we show how this theory can be adapted to account for vibrationally induced photodetachment. In particular, we explain how the single attractive rotationally adiabatic curve for the $e^- + AB(v=1)$ interaction can cross the repulsive rotationally adiabatic potential-energy curves for the $e^- + AB(v=0)$ interaction to produce the electron detachment. Furthermore, we use a simple Franck-Condon theory to show that, for large J, the curve crossing probabilities and photodetachment linewidths become smaller as J increases. Section IV applies the simple semiquantitative results obtained to the PtN^- photodetachment and results for the J dependence of the linewidths are compared with experiment.[10] Conclusions are in Sec. V.

II. ROTATIONALLY ADIABATIC THEORY

We describe the rotationally adiabatic theory for the photodetachment of electrons from diatomic dipolar negative ions including vibrational motion. Our previous application of the theory[7] to symmetric top and slightly

asymmetric top molecules ignored vibrational effects. We assume that the system can be described by an $e^- + AB$ interaction with the rotational levels of AB being used in a basis set appropriate for electron-molecule scattering with a space-fixed system of coordinates. As we are interested in what is essentially an electron scattering problem with an energy just above threshold, and as we also assume that the AB molecule has a large dipole moment, it is reasonable to consider the potential-energy surface for the problem as just the long-range interaction

$$V(R,r,\theta) = -f(R)\alpha/(2R^4) + \mu_D(r)\cos\theta/R^2 . \quad (1)$$

Here α is the isotropic polarizability of the molecule, $\mu_D(r)$ is the dipole moment function of the diatomic molecule that depends on the AB bond distance r, and θ is the angle that the vector $\mathbf{R}$ from the electron to the center of mass of the molecule makes with the direction of the dipole. Also $f(R)$ is a suitably chosen damping function that is needed to prevent the potential from diverging near the origin. In our previous calculations[7] on both CH_2CN^- and CH_2CHO^- we found that the function

$$
\begin{aligned}
f(R) &= -\infty, \quad R=0 \\
f(R) &= 1 - \exp[-(R/2)^6]
\end{aligned}
\quad (2)
$$

was suitable. Note that R and all variables are in atomic units in this paper, except where stated. We are ignoring the explicit treatment of short-range and exchange effects, but these effects will not be significant for understanding the rotational structures in the photodetachment spectra. Furthermore, we are assuming that the r dependence of $\mu_D(r)$ is the driving force for the vibrationally induced electron detachment and the r dependence of α and f can be neglected. It is also useful to define the matrix elements

$$\mu_{vv'} = \langle v|\mu_D(r)|v'\rangle ,$$

where $|v\rangle$ is the vibrational wave function for level v of AB. For previous theoretical work on electron-dipole bound and scattering states see Refs. 15–35.

With the potential of Eq. (1) and other approximations discussed above, the Hamiltonian for the $e^- + AB(v)$ interaction in vibrational state v is approximated by

$$H = b_v \mathbf{j}^2 + l^2/(2R^2) + V(R,r,\theta) + E_v , \quad (3)$$

where b_v is the rotor constant for the diatomic molecule for vibrational state v, $\mathbf{j}^2$ is the molecular rotational angular momentum operator, and l^2 is the orbital angular momentum operator of the electron. We are using a space-fixed system of coordinates and an appropriate angular basis set to use is[36]

$$\mathcal{Y}_{jlJM} = \sum_{m_j m_l} C(j,l,J,m_j,m_l,M)$$

$$\times Y_{jm_j}(\theta',\phi')Y_{lm_l}(\theta'',\phi'') , \quad (4)$$

which are eigenfunctions of the total angular momentum

operator $\mathbf{J}^2$ of the $e^- + AB$ system. Here, the C's are Clebsch-Gordan coefficients, (θ',ϕ') and (θ'',ϕ'') are the spherical polar angles describing, respectively, the orientation of the AB internuclear vector $\mathbf{r}$ and $\mathbf{R}$ in the space-fixed system of coordinates, and the Y's are the

spherical harmonics.

For a fixed value of the total angular momentum J, we then diagonalize on a grid of R values the Hamiltonian of Eq. (3) using these basis functions. The Hamiltonian matrix to diagonalize is

$$H_{vjlj'l'} = [b_v j(j+1) + l(l+1)/(2R^2) - f(R)\alpha/(2R^4) + E_v]\delta_{jj'}\delta_{ll'}$$

$$+ (\mu_{vv}/R^2)[(2j+1)(2j'+1)(2l+1)(2l'+1)]^{1/2}(-1)^{j+j'-J}\begin{pmatrix} l & l' & 1 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} j & j' & 1 \\ 0 & 0 & 0 \end{pmatrix}\begin{Bmatrix} j' & l' & J \\ l & j & 1 \end{Bmatrix}, \qquad (5)$$

where the terms in large parentheses are the $3j$ Wigner symbols and those in large curly brackets are the $6j$ Wigner symbols. This yields a set of eigenvalues that can be adiabatically connected to produce a set of rotationally adiabatic potential curves $\varepsilon_{(vjlJ)}(R)$. These are labeled by the asymptotic state to which each level tends as R gets large such that

$$\varepsilon_{(vjlJ)}(R) \rightarrow E_v + b_v j(j+1) + l(l+1)/(2R^2). \qquad (6)$$

Thus the (v,j,l,J) quantum numbers are used to label these "rotationally adiabatic" potential curves. An analytical approximation[37] suggests that the dipole moment must be as large as $(15)^{1/2}$ atomic units or 9.84 D to give more than one attractive adiabatic potential for a given J, and many computations we have performed have verified this.[7,37] Therefore for dipole moments smaller than this, only one rotationally adiabatic potential curve is attractive and this one correlates with $j=0, l=J$, i.e., it is $\varepsilon_{(v0JJ)}(R)$. An example of the calculated rotationally adiabatic potential-energy curves for the $e^- + CH_2CN$ interaction with $J=30$ and $K=0$ is shown in Fig. 1.

For values of J greater than 0, the attractive rotationally adiabatic potential $\varepsilon_{(v0JJ)}(R)$ does have a centrifugal barrier and therefore cannot only support bound states, but can also support shape resonances corresponding to a temporary trapping of a dissociating electron inside the centrifugal barrier. These bound and resonance states can both be calculated by solving numerically the one-dimensional Schrödinger equation

$$[-\tfrac{1}{2}d^2/dR^2 + \varepsilon_{(v0JJ)}(R)]\chi_{vJ}(R) = E\chi_{vJ}(R), \qquad (7)$$

with appropriate boundary conditions. Here E is the collision energy. For efficient photodetachment of an electron, the translational wave function $\chi_{vJ}(R)$ of the dissociating state must have a good overlap with that for the original bound anion ground state. This will occur for those special energies associated with scattering resonances when there is an appreciable probability density in the shorter-range region where the bound-state wave functions are localized. Therefore the energies and widths of the shape resonances can be identified with the positions and widths of the lines in the photodetachment spectra.[7] Feshbach resonances arise through transitions between two different adiabatic curves.[38] In this case,

one rotationally adiabatic curve can support a bound state, and the other a scattering state.

In our previous work,[7] we analyzed the rotationally adiabatic curves for the interaction of electrons with symmetric and asymmetric top molecules in their vibrational ground states. The regular rotational structure in the photodetachment spectra for dipolar symmetric tops such as CH_2CN^- was identified with the shape resonances that could occur on the one attractive rotationally adiabatic potential curve obtained for each value of J. In the case of asymmetric top negative ions such as CH_2CHO^-, Feshbach resonances also occur through $\Delta K = -1$ transitions between rotationally adiabatic curves labeled by the approximate symmetric top projec-
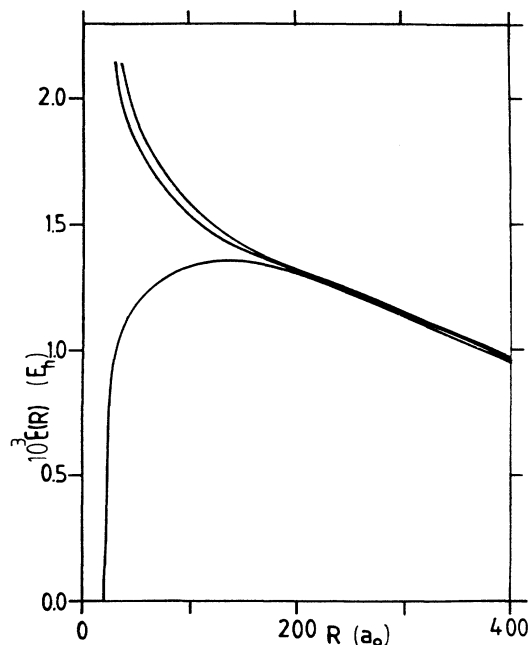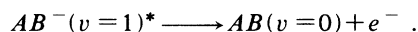

FIG. 1. Rotationally adiabatic curves for the $e^- + CH_2CN$ interaction with $J=30$ and $k=0$. The dipole moment of CH_2CN used in the calculations was 3.71 D.

tion quantum numbers K. The analysis of these Feshbach resonances gave a linewidth formula that had a K dependence of $(a - b)^2(2K - 1)^2$, where a and b are rotor constants, and this dependence was shown to hold quite well not only in experiments[6] on CH_2CHO^-, but also in subsequent experiments[9] on CD_2CDO^-. Solutions of Eq. (7) and calculations of the resonance positions and widths gave near quantitative agreement[7] with the measured[5,6,9] photodetachment spectra for CH_2CN^-, CD_2CN^-, CH_2CHO^-, and CD_2CDO^-. These extensive comparisons between theory and experiment demonstrate the usefulness of applying the rotationally adiabatic theory to the interpretation of photodetachment experiments.

III. VIBRATIONALLY INDUCED PHOTODETACHMENT

In the present paper, we are interested in the photodetachment spectra corresponding to the electron detachment process

$$AB^-(v = 1)^* \longrightarrow AB(v = 0) + e^- \ .$$

The attractive rotationally adiabatic potential $\varepsilon_{(v=1, j=0, l=J,J)}(R)$ for the $v = 1$ state can support bound states or shape resonances but it is crossed by *repulsive* rotationally adiabatic curves for the $v = 0$ state such as $\varepsilon_{(v=0, j=1, l=J-1,J)}(R)$. Thus if the curve crossing has an appreciable probability, vibrational relaxation (i.e., a $v = 1 \rightarrow 0$ transition) can occur and the AB molecule can be produced in the $v = 0$ state and the electron will have sufficient energy to detach. The width of this Feshbach resonance can be associated with a linewidth in the photodetachment spectra, while the line positions can be identified with the energies of the bound or shape resonance states for the $v = 1$ rotationally adiabatic potential $\varepsilon_{(v=1, j=0, l=J,J)}(R)$. This mechanism is illustrated in Fig. 2 where the $v = 0$ attractive rotationally adiabatic curve of Fig. 1 is displaced by one quantum of vibrational energy. The rest of this section is devoted to the derivation of an approximate formula that gives the J dependence of the linewidth for this particular type of Feshbach resonance.

For a given value of J, Fig. 3 shows the bound-state energy E_{bJ} on the attractive $v = 1$ rotationally adiabatic curve and the crossing point $R = R_{xJ}$ at energy E_{xJ} for the attractive $v = 1$ and repulsive $v = 0$ curves. A similar diagram can be drawn for each value of J. If there is a shape resonance on the $v = 1$ curve, and not a bound state, then E_{bJ} refers to the resonance energy. Note that the crossing energy E_{xJ} is in the classically forbidden region of the wave function with energy E_{bJ} (i.e., $E_{xJ} > E_{bJ}$). The wave function on the $v = 1$ curve with energy E_{bJ} is $\chi_{1J}(R)$ and that for the repulsive $v = 0$ curve at energy E_{bJ} is $\chi_{0J}(R)$. We can then apply a Franck-Condon approximation in which it is assumed that it is necessary to treat only the overlap between wave functions accurately in the region close to R_{xJ}. The linewidth for the vibrationally induced photodetachment is then approximated[39] by

$$\Gamma_J = 2\pi[(\mu_{10})^2/R_{xJ}^4]|\int_0^\infty \chi_{1J}(R)\chi_{0J}(R)dR|^2 \ . \tag{8}$$
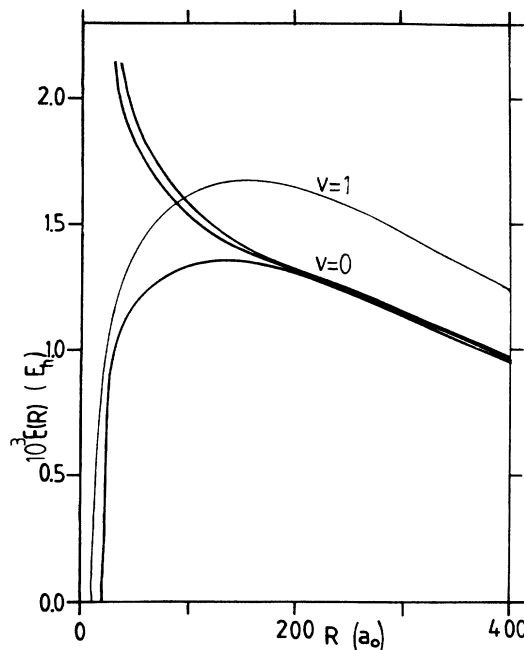

FIG. 2. Rotationally adiabatic curves as for Fig. 1, but including the $v = 1$ attractive curve which is displaced from the $v = 0$ curve by one quantum of vibrational energy.

Here, we assume that it is the matrix element

$$\mu_{10}/R_{xJ}^2 = \langle v = 1|\mu_D(r)|v' = 0\rangle /R_{xJ}^2$$

that induces the vibrational relaxation.

We now need to derive formulas for the wave functions in Eq. (8) so that the Franck-Condon integral can be evaluated. It is appropriate to apply the Airy function approximations[38,39]

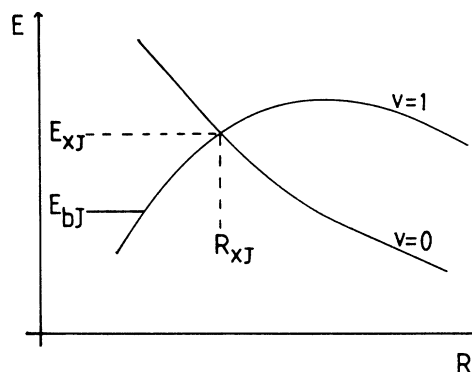$$\chi_1(R) = (2\omega_1/\alpha_{1J})^{1/2}Ai(-\alpha_{1J}(R - a_{1J})) \tag{9}$$

FIG. 3. Illustration of the crossing between the $v = 1$ attractive rotationally adiabatic potential curve and a repulsive curve for the $v = 0$ state. Here E_{bJ} is the bound-state energy for the $v = 1$ attractive curve, while the $v = 1$ and repulsive $v = 0$ curves cross at $R = R_{xJ}$ with energy E_{xJ}.

and

$$\chi_0(R) = (2/\alpha_{0J})^{1/2} \text{Ai}(-\alpha_{0J}(R - a_{0J})) , \qquad (10)$$

where Ai is an Airy function, ω_1 is the local energy-level spacing for the $v = 1$ rotationally adiabatic curve, a_{1J} is the inner classical turning point on the $v = 1$ curve for energy E_{bJ}, a_{0J} is the classical turning point on the repulsive $v = 0$ curve at energy E_{bJ}, and $\alpha_{vJ} = (2F_{vJ})^{1/3}$, where

$$F_{vJ} = -\left[\frac{d\varepsilon_{vJ}(R)}{dR}\right]_{R = R_{xJ}} . \qquad (11)$$

Here $\varepsilon_{vJ}(R)$ is the appropriate rotationally adiabatic curve for vibrational state v and a linear expansion of $\varepsilon_{vJ}(R)$ about $R = R_{xJ}$ has been assumed.

Substitution of these wave-function expressions into Eq. (8) gives

$$\Gamma_J = \tfrac{1}{4}\Gamma_J^0 \exp\{-\tfrac{4}{3}[(E_{xJ} - E_{bJ})/E_J^*]^{3/2}\} , \qquad (12)$$

where

$$\Gamma_J^0 = |4\omega_1[(\mu_{10})^2/R_{xJ}^4]/(v_J \Delta F_J)| , \qquad (13)$$

$$v_J = [2(E_{xJ} - E_{bJ})]^{1/2} , \qquad (14)$$

$$\Delta F_J = F_{1J} - F_{0J} , \qquad (15)$$

and

$$E_J^* = [F_{1J}^2 F_{0J}^2/(2\Delta F_J^2)]^{1/3} . \qquad (16)$$

The expansion of the Airy functions in terms of exponential functions follows[39] since E_{bJ} is less than E_{xJ} and the contribution to the Franck-Condon integral comes from the classically forbidden region of $\chi_1(R)$.

In a previous paper[37] on the chemical reaction between an electron and a dipolar molecule we showed that analytical formulas could be derived for the two lowest energy rotationally adiabatic curves at the region near the centrifugal maximum in the potential-energy curve. This is because, in this region, the expansion of Eq. (4) is dominated by just the two basis functions with ($j = J$, $l = 0$) and with ($j = J - 1$, $l = 1$). This gives a 2×2 secular equation problem to solve, which gives the formula[37]

$$\varepsilon_{vJ}(R) = E_v + \tfrac{1}{2}(2b_v J^2 + 1/R^2)$$
$$\pm [\tfrac{1}{4}(2b_v J - 1/R^2)^2 + \mu_{vv}^2/(6R^4)]^{1/2} \qquad (17)$$

for the adiabatic potential-energy curves with the lowest two energies for vibrational state v and large values of the total angular momentum J. For large values of the dipole moment matrix element μ_{vv} this gives the simple formulas for the attractive $v = 1$ and repulsive $v = 0$ rotationally adiabatic potential curves

$$\varepsilon_{1J}(R) = E_1 + b_1 J^2 + 1/(2R^2) - D/R^2 \qquad (18)$$

and

$$\varepsilon_{0J}(R) = b_0 J^2 + 1(2R^2) + D/R^2 , \qquad (19)$$

where the energy zero has been set to $E_0 = 0$ and

$$D = \mu/6^{1/2} , \qquad (20)$$

where μ is the modulus of the average of μ_{11} and μ_{00}.

At the crossing point $R = R_{xJ}$ we have that

$$\varepsilon_{1J}(R_{xJ}) = \varepsilon_{0J}(R_{xJ}) = E_{xJ} ,$$

and Eqs. (18) and (19) are equated to give

$$D/R_{xJ}^2 = \tfrac{1}{2}[E_1 + (b_1 - b_0)J^2] . \qquad (21)$$

Upon substituting back for R_{xJ}, and assuming that $D \gg \tfrac{1}{2}$, we have

$$E_{xJ} = \tfrac{1}{2}(b_1 + b_0)J^2 + E_1/2 . \qquad (22)$$

Furthermore, it is trivial to evaluate the derivatives

$$F_{1J} = -\left[\frac{d\varepsilon_{1J}(R)}{dR}\right]_{R = R_{xJ}} = 2D/R_{xJ}^3 \qquad (23)$$

and

$$F_{0J} = -\left[\frac{d\varepsilon_{0J}(R)}{dR}\right]_{R = R_{xJ}} = -2D/R_{xJ}^3 \qquad (24)$$

so that

$$\Delta F_J = 4D/R_{xJ}^3 \qquad (25)$$

and

$$E_J^* = [F_{1J}^2 F_{0J}^2/(2\Delta F_J^2)]^{1/3}$$
$$= [1/(16D)^{1/3}][E_1 + (b_1 - b_0)J^2] . \qquad (26)$$

In our previous paper on photodetachment we showed that the energy E_{bJ} is given by

$$E_{bJ} = -G + b_1 J(J + 1) + E_1 , \qquad (27)$$

where the constant G does not depend on J, but does depend on the shorter-range part of the potential-energy surface [see Eq. (14) in Ref. 7]. We therefore have that

$$E_{xJ} - E_{bJ} = \tfrac{1}{2}(b_0 - b_1)J^2 - b_1 J + G - E_1/2 . \qquad (28)$$

These equations enable the linewidth formula of Eq. (12) to be expressed as

$$\Gamma_J = Af_J^{-1/2}\exp(-Bf_J^{3/2}) , \qquad (29)$$

where

$$A = w_1\mu_{10}^2/[8(\mu/6^{1/2})^{3/2}] , \qquad (30)$$

$$B = \tfrac{16}{3}(\mu/6^{1/2})^{1/2} , \qquad (31)$$

and

$$f_J = [(\Delta b/2)J^2 - b_1 J + G - E_1/2]/(E_1 - \Delta bJ^2) , \qquad (32)$$

with

$$\Delta b = b_0 - b_1 . \qquad (33)$$

Therefore we have expressed the linewidth for the photodetachment process as a relatively simple function which has a very clear dependence on the rotor constants b_1 and b_0 and the total angular momentum quantum number J. For small values of J, the function f_J will decrease with increasing J. However, for large values of J,

f_J will eventually increase with J as Δb will normally be positive. Thus the exponential function of the linewidth formula (29) will decrease with increasing J for large J, and this will dominate the pre-exponential factor.

The theory therefore predicts that the photodetachment linewidths will decrease with increasing J for large values of J. This result is related directly to the fact that the rotor constant for the $v = 1$ state is smaller than that for the $v = 0$ state so that Δb is positive. Referring back to Eq. (28), it can be seen that the difference in energy between E_{xJ} and E_{bJ} gets larger as J increases for large values of J. This means that the overlap between the wave functions on the $v = 1$ and $v = 0$ rotationally adiabatic potential-energy curves will diminish as J increases; the larger the difference between E_{bJ} and E_{xJ}, the weaker the overlap will be. If Δb was zero, then this unusual J effect would not arise.

IV. APPLICATION TO PtN⁻

It is appropriate to apply the theory described in Sec. III to the photodetachment in PtN⁻. This is because rotationally resolved photodetachment spectra[10] have been reported for this system, with linewidths being measured for $44 < J < 58$. By repeating the experiments with isotopically substituted PtN, it was established that the mechanism for photodetachment is

$$PtN^- \xrightarrow{h\nu} PtN^-(v=1)^* \longrightarrow PtN(v=0)+e^- \ .$$
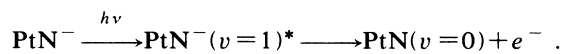
This is exactly the process discussed in Sec. III. Knowledge of the accurate electron affinity for PtN established that the product was PtN ($v = 0$) for the transition energies studied.[10] The linewidths for $J < 45$ were too broad to measure. With $J > 58$ the lifetime of the PtN⁻($v = 1$) is so long ($> 10 \ \mu s$), that there is not enough time for the electron to detach in the experimental apparatus. Therefore linewidths could not be measured for $J > 58$.

Unfortunately, the dipole moment function is not known for PtN. However, several *ab initio* calculations[40] have been performed on similar diatomics containing transition metal atoms, and these calculations have invariably given very large dipole moments and large dipole derivatives with respect to the vibrational coordinate. The theory outlined in Sec. III involves several approximations, and is not intended to be a quantitative theory for absolute linewidths. Rather, it is useful in explaining trends such as how the photodetachment linewidths will depend roughly on J and the rotor constants for the ground and excited vibrational states of the parent neutral molecule. It therefore seems reasonable to apply our photodetachment formula of Eq. (29) to PtN⁻ assuming certain molecular parameters; if these parameters are considerably in error it is unlikely that the general trends will change.

We choose the parameter A in Eq. (29) to reproduce the experimental[10] linewidth of 2.6 GHz at $J = 45$. Also the G parameter in Eq. (28) is chosen so that $f_J = 0$ at $J = 44$, where the linewidth becomes too large to measure. We also use the experimentally estimated[10] parameters $E_1 = 100$ cm^{-1} for the vibrational energy, and $b_0 = 0.45$ cm^{-1} and $b_1 = 0.40$ cm^{-1} for the rotational constants. This gives a G value of 39.4 cm^{-1}. Furthermore, we use a value of $\mu = 3.0$ D for PtN, although the overall J dependence of the linewidth is not extremely sensitive to the magnitude of the dipole moment. In fact, the only parameters that the linewidths are really sensitive to are the rotor constants b_1 and b_0, which can be estimated quite accurately from the experiment.

In Fig. 4 we plot the photodetachment linewidth obtained with these parameters substituted into Eq. (29). The results are compared to those measured[10] for the R and Q branches in PtN⁻. It can be seen that the overall dependence of the linewidths on J is obtained quite well in the calculations, with a significant drop in linewidth as J increases beyond $J = 44$. Considering the many approximations made in the derivation, and the uncertainties in the parameters used, the comparison between theory and experiment must be considered to be quite promising. The results give evidence to support the simple curve crossing model for explaining the unusual decrease in the linewidths for increasing J.

An alternative and more simple model has been proposed[10] to explain the photodetachment spectra for PtN⁻ and CH₂CN⁻. This "channel-opening theory" involves examining the product molecular rotational channels which become open when J is increased and considering whether angular momentum quantum number changes will allow transitions into these states. Unlike the rotationally adiabatic theory described in the present paper, this model does not explain how the sharp lines (i.e., resonances) in the photodetachment spectra occur and does not take into account the detailed dynamics of the electron-molecule interaction. However, it is a simpler model than the one described here, although the rotation-
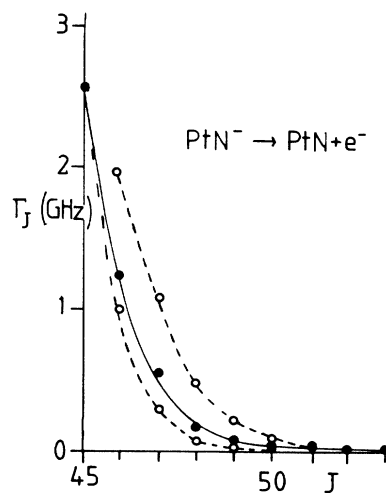

FIG. 4. Calculated photodetachment linewidths for model PtN⁻ (solid circles). Also shown are the experimental (Ref. 10) measurements for the Q branch (upper dotted curve) and R branch (lower dotted curve) of PtN⁻. Note that the calculations have been normalized to the experimental linewidth at $J = 45$.

ally adiabatic theory does produce a clear picture for the mechanism of photodetachment. So far, the channel-opening theory has not been formulated mathematically to yield formulas for the photodetachment linewidths, whereas such formulas have been derived for the rotationally adiabatic theory.

To examine the relationship between these two approaches, it is instructive to see how they relate to an exact calculation of the photodetachment linewidth. In principle, an exact calculation can be done by solving the full close-coupling equations[30] obtained with the basis set of Eq. (4). Our rotationally adiabatic approach is closely related to the close-coupling method in that we do diagonalize, as a function of R, the close-coupling matrix of Eq. (5). Furthermore, we consider explicitly the detailed quantum-mechanical scattering wave functions on the rotationally adiabatic potential curves. However, once the rotationally adiabatic curves are calculated we do not let transitions occur between those for a particular vibrational state as we assume that the photodetachment spectra are dominated by the resonance or bound state on just the one attractive curve. Thus our theory, as it stands, does not give information on the most likely rotational state of the molecule that is produced after the photodetachment and boundary conditions are not applied to the wave function with the full number of final rotational states. In a certain sense the channel-opening theory does take the final-state energetics into detailed account, although it does, essentially, ignore the dynamics of the autodetachment process.

The reason why both theories seem to account for the J dependence of the photodetachment linewidths in PtN$^-$ is probably related to the fact that the asymptotic rotational energies arise in a very simple way in the expressions for the rotationally adiabatic potential curves and the resonance and bound-state energies for these curves [see Eqs. (18) and (27)]. Furthermore, both theories explain the J dependence in terms of the different rotor constants for the $v=0$ and $v=1$ states. However, for systems such as CH$_2$CN$^-$ and CH$_2$CHO$^-$, the rotationally adiabatic theory correctly accounts quantitatively[7] for the trends in the dependence of the linewidths on J and K and also gives realistic predictions for isotope effects. It is unclear if the channel-opening approach can account for these subtle effects. However, a hybrid of the rotationally adiabatic and channel-opening theories might relate more closely to the exact close-coupling solutions and might prove fruitful in predicting the product molecular rotational distributions produced from the autodetachment process.

It is important to relate the rotationally adiabatic theory to the Born-Oppenheimer approximation. The Born-Oppenheimer approximation separates electronic from nuclear motion and is justified by the assumption that electrons normally move much faster than molecular vibrations and rotations. The rotationally adiabatic theory that we have described couples together explicitly the orbital angular momentum of the electron and the rotational angular momentum of the molecule to give total angular eigenfunctions of the whole electron-molecule system. Thus the Born-Oppenheimer approximation is

not applied to the *angular* motion of the electron. However, the ability of the radial motion of the electron to induce transitions from one rotationally adiabatic curve to another is ignored. This can be justified in the special case of the photodetachment of electrons from negative molecular ions with large dipole moments as the electron is detaching with an energy very close to threshold and has to tunnel through the centrifugal barrier in the rotationally adiabatic potential. Thus the electron is moving in this region on a slow time scale compared to the vibrational and rotational motion. Furthermore, the frequency associated with the rotational motion of the molecule is much enhanced by the strongly anisotropic potential of the electron-dipole interaction. Thus the angular and vibrational motion of the electron-molecule system, and the radial motion of the electron, will not have similar time scales that enable these motions to come into resonance so that rotational transitions can be easily induced to invalidate the rotationally adiabatic theory. We should emphasize also that there are kinetic energy terms in the Hamiltonian that couple the molecular vibrational motion with the electron motion and which can contribute to the photodetachment linewidth.[13] These terms have been ignored in the present theory which assumes that it is the vibrational-rotational dependence of the electron-dipole potential energy that is the major factor in producing the rotational structure in the photodetachment linewidths. The kinetic energy matrix elements will add an extra background linewidth to those produced from the potential-energy terms, although it seems unlikely that they can produce the unusual rotational structures observed. However, further research on this is needed.

An alternative theory for the autodetachment of electrons from molecular negative ions has recently been proposed by Russek,[41] based on methods used in nuclear physics. It is unclear whether this theory can be easily applied to the vibrationally induced electron detachment problem or can provide a deeper understanding of the subtle rotational linewidth dependences in polyatomic ions such as CH$_2$CN$^-$ and CH$_2$CHO$^-$. Nor is it clear if this theory can provide simple pictures and formulas for the photodetachment process, which arise naturally out of the rotationally adiabatic theory.

V. CONCLUSION

We have presented an analytical theory for describing the J dependence of linewidths for the photodetachment of electrons from dipolar negative molecular ions when vibrational relaxation occurs as part of the autodetachment process. The theory provides a simple picture for explaining how the observed photodetachment linewidths for PtN$^-$ decrease with increasing J.

The theory is based on the use of rotationally adiabatic potential curves that are obtained by diagonalizing a simple electron-dipole interaction potential with a basis set appropriate for the rotationally inelastic scattering of an electron with a polar diatomic molecule. The fact that a repulsive rotationally adiabatic potential curve for the $v=0$ state crosses the attractive curve for the $v=1$ state

is exploited to yield a simple formula for the photodetachment linewidth. This formula predicts that, for large J, the linewidths decrease with increasing J. This dependence on J is directly related to the rotational constant for the $v=1$ state having a smaller value than that for the $v=0$ state. As J increases, this gives an increasing difference in the bound-state energy on the $v=1$ rotationally adiabatic curve and the energy at the crossing point for the $v=0$ and $v=1$ curves. Thus the overlap of the wave functions for the $v=1$ and $v=0$ rotationally adiabatic potential curves will decrease as J increases. Hence the linewidth for photodetachment, which depends on this overlap, will also decrease as J increases.

Previous applications[7] of the rotationally adiabatic theory to the photodetachment of electrons from polyatomic dipolar negative ions in vibrational ground states have also been successful in explaining quantitatively the dependencies of the linewidths on the rotational quantum numbers J and K for systems such as CH_2CN^- and CH_2CHO^- and also the effects of isotopic substitution in these ions. The fact that the theory can also provide an explanation for the more unusual linewidths in PtN^- demonstrates again the usefulness of this approach for understanding the mechanism of autodetachment in terms of the dynamics of the electron-dipole interaction. Not only does the theory provide useful formulas, but it also gives a simple picture for the photodetachment process that can rationalize seemingly unusual experimental results.

ACKNOWLEDGMENTS

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