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INTERPRETATION OF THE SHIFT IN THE MAXIMA OF RESONANCE CROSS SECTION
FOR VIBRATIONAL EXCITATION OF MOLECULES BY ELECTRONS

by

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University of Colorado
Boulder, Colorado
April 12, 1966

On page 29, there is an error in Table A1, which should read

\[ c_8 = 3.066785 \times 10^{-4} \]
\[ c_9 = 2.367851 \times 10^{-5} \]
\[ c_{10} = 7.862225 \times 10^{-7} \]

and on page 28, in Eq. (A10), the upper limit of summation should be 10 instead of 9. The correct values were used in all the calculations reported in the paper.
INTERPRETATION OF THE SHIFT IN THE MAXIMA OF RESONANCE CROSS SECTION
FOR VIBRATIONAL EXCITATION OF MOLECULES BY ELECTRONS

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ABSTRACT

In vibrational excitation of molecules by electrons, we observe that the maxima of the resonance cross section is shifted to higher energies when the vibrational quantum number \( v \) being excited is increased. We show that the reason for this shift is due to the changes in magnitudes of the nuclear matrix elements in the transition matrix which are very sensitive functions of the vibrational quantum numbers. The positions of the resonances, which correspond to the poles in the transition matrix and to the vibrational structure of the compound state, do not shift at all when \( v \) being excited is increased. This is consistent with the proposed excitation mechanism which involves compound negative-ion states as intermediates. A numerical example is given for the case of vibrational excitation of nitrogen molecules by electrons.

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I. INTRODUCTION

In the cross section for vibrational excitation of molecules such as $N_2$ by electrons, one observes several resonance peaks which are interpreted as coming from the vibrational structure of a compound state of the parent negative molecular ion. The maxima of these peaks seem, however, to move to higher energies with the increase in the vibrational quantum number $v$ of the target molecule being excited. This latter observation is apparently not consistent with the excitation mechanism in which the vibrational excitation proceeds via compound negative-ion states as intermediates. The purpose of this note is to provide an interpretation of this shift and to show that it is consistent with the proposed excitation mechanism.

In the next section we show that the reason the maxima of the peaks shift is because of the changes in magnitudes of the nuclear matrix elements in the transition matrix which are very sensitive functions of the vibrational quantum numbers. The positions of the resonances which correspond to the poles in the transition matrix and to the vibration structure of the compound state, do not shift at all with the increase of vibrational quantum number $v$ being excited. This is consistent with the proposed excitation mechanism involving compound negative-ion states as intermediates. A numerical example is also given in this section for vibrational excitation of nitrogen molecules by electrons.
II. THEORETICAL INTERPRETATION

The cross section for resonance vibrational excitation of molecules by electrons can, for an isolated resonance, be written within the Born-Oppenheimer approximation with rotational motion suppressed, as (in atomic units)

\[
\sigma(v \rightarrow v') = f_{vv'}(E) \left| \sum_{\lambda} \frac{\langle x_{v'} | \xi_\lambda^* \xi_\lambda | x_v \rangle}{(E - \xi - \lambda \omega_e + i \frac{1}{2} \Gamma_\lambda)^2} \right|^2
\]

(1)

where the \( x_v \)'s and the \( \xi_\lambda \)'s are the vibrational wave functions respectively of the target molecule in a given electronic state and of the negative ion in an isolated compound electronic state, where \( \xi \) is the electronic resonance energy plus the zero-point energy \( \frac{1}{2} \omega_e \) of the compound state, and where the \( \Gamma_\lambda \)'s are the resonance widths. The function \( f_{vv'}(E) \) is a slow varying function of the incident electron energy in the neighborhood of the resonance energy. The general Breit-Wigner expression [Eq. (1)] for the cross section is valid within the mentioned approximations regardless of how it is formulated.

Equation (1) may be rewritten as

\[
\sigma(v \rightarrow v') = f_{vv'}(E) \left\{ \left[ \frac{1}{2} \sum_{\lambda} \frac{\Gamma_\lambda \langle x_{v'} | \xi_\lambda^* \xi_\lambda | x_v \rangle}{(E - \xi - \lambda \omega_e)^2 + \frac{1}{4} \Gamma_\lambda^2} \right]^2 + \left[ \sum_{\lambda} \frac{(E - \xi - \lambda \omega_e) \langle x_{v'} | \xi_\lambda^* | x_v \rangle}{(E - \xi - \lambda \omega_e)^2 + \frac{1}{4} \Gamma_\lambda^2} \right]^2 \right\}
\]

(2)

It is then clear that at incident electron energies \( E = \xi, \xi + \omega_e, \xi + 2\omega_e, \ldots \) etc., the corresponding terms in the first bracket give rise to
resonances and are exactly zero in the second bracket. The relative magnitudes of the cross section depend strongly on the products \( \langle x_v, | \xi_\lambda \rangle \langle \xi_\lambda | x_v \rangle \) and their corresponding energy term \( (E - \xi + \lambda \omega_e)^2 + \frac{1}{4} \left< \tilde{t} \right>^2 \) in the denominator.\(^3\) It can be shown that the resonance width is primarily a property of the electronic structure so that we may suppress its weak dependence on nuclear state \( \lambda \) by defining an averaged width \( \left< \tilde{t} \right> \). The magnitudes of the cross section at various resonances \( E = \xi + \lambda \omega_e \) with \( \lambda = 0, 1, 2, \ldots \), take the expression

\[
\left[ \sigma(v + v') \right]_{E = \xi + \lambda \omega_e} = f_{vv'}, (\xi + \lambda \omega_e) \left\{ \sum_{\lambda} \frac{2}{\langle \tilde{t} \rangle^2 + 4(\lambda - \lambda')^2 \omega_e^2} \left[ \langle x_v | \xi_\lambda \rangle \langle \xi_\lambda | x_v \rangle \right]^2 \right\}^2 \right.
\]

\[
+ \sum_{\lambda, \lambda' \neq \lambda} \frac{2}{(\lambda - \lambda')^2 \omega_e^2} \left[ \langle x_v | \xi_\lambda \rangle \langle \xi_\lambda | x_v \rangle \right]^2 \left[ \langle x_v | \xi_{\lambda'} \rangle \langle \xi_{\lambda'} | x_v \rangle \right]^2 \}
\right.
\]

\[
(3)
\]

For cases where \( \langle \tilde{t} \rangle < \omega_e \), the resonance cross section can be approximated by the leading term in Eq. (3):

\[
\left[ \sigma(v + v') \right]_{E = \xi + \lambda \omega_e} \approx \frac{4}{\langle \tilde{t} \rangle^2} f_{vv'}, (\xi + \lambda \omega_e) \left[ \langle x_v | \xi_\lambda \rangle \langle \xi_\lambda | x_v \rangle \right]^2
\]

\[
(4)
\]

This demonstrates clearly that at incident electron energies corresponding to the positions of resonances \( E = \xi + \lambda \omega_e \), the relative magnitudes of the cross section for the excitation of \( v \) to \( v' \) is governed primarily by the nuclear matrix elements \( \left[ \langle x_v | \xi_\lambda \rangle \langle \xi_\lambda | x_v \rangle \right]^2 \), the magnitudes of which
depend very sensitively on both nuclear states \( v' \) and \( \lambda \). When the magnitude of the nuclear matrix element approaches zero, the corresponding resonance cross section becomes quite small and is no longer observable within the experimental resolution. This dependence also accounts for the observed energy loss spectrum at various incident electron energy.\(^5\)

In Table I, we have tabulated the values of the nuclear matrix elements for vibrational excitation of the ground state of \( \text{N}_2 \) molecules at various incident electron energies corresponding to the resonance positions. The molecular constants for the negative-ion state are taken from those determined approximately in a previous semiempirical calculation.\(^3,6\)

By examining the relative magnitudes of the matrix elements, we are able to explain the changes in relative heights of the cross sections for different vibrational states excited at various resonance energies, and to explain the disappearance of the first few resonances with the increase in the vibrational quantum number being excited (Fig. 1). The approximate positions of the resonance\(^3\) are indicated by dashed lines in Fig. 1. The points where these lines intersect the experimental curve indicate the relative magnitudes of the cross section at these resonances. The ratios of the cross sections for exciting different vibrational states agree fairly well with the ratios of the corresponding nuclear matrix elements. Because the averaged width \( \langle P \rangle \approx 0.152 \text{ eV} \) is comparable in magnitude with the energy spacing of the compound system \( \sim 0.23 \text{ eV} \), the maxima of the cross section do not coincide with the positions of the resonance. The combined effects of this behavior result in the shift in the maxima of the cross section. The predicted pattern for the shift of the maxima to higher energies with the increase in quantum number \( v \) being excited [shown in
Table I by the diagonal heavy lines] agrees very well with the experimental observations shown in Fig. 1. The positions of the resonances are, of course, not shifted at all. This is entirely consistent with the proposed excitation mechanism involving compound negative-ion states as intermediates.

ACKNOWLEDGMENT

The author is grateful to Dr. Ugo Fano for encouraging him to write this interpretation.


4. For simplicity we take the linear harmonic oscillator approximations for nuclear states of the compound system.


6. In Ref. 3(a), we have found that the set of molecular constants needed for the excited field of the target molecule is very similar to that of the $x^1\Sigma^-$ state of $N_2$. It is misleading to interpret this finding as an indication that the excited field of the target molecule is generated solely by the $x^1\Sigma^-$ state of $N_2$. Rather, it should be interpreted that the similarity between the set of molecular constants and that of the $x^1\Sigma^-$ state is coincidental. The set of molecular constants thus really describes an effective molecular field created by virtual excitations of the target molecule in which the projectile electron propagates. It should be noted that the effective molecular field also contains a substantial component of the ground electronic state of the target molecule with excited nuclear vibrational and rotational states [Ref. 3(b)].
Table 1. Calculated Values\(^a\) for the Nuclear Matrix Elements \(\langle \chi_{v'} \mid \xi_{\lambda} \rangle \langle \xi_{\lambda} \mid \chi_v \rangle \)\(^2\) which are Related to the Cross Section for Vibrational Excitation of Nitrogen Molecules at Incident Electron Energy

\[ E = \xi + \lambda \omega_e \left[ 1 - (\lambda+1) x_e \right] \] \(^b\)

<table>
<thead>
<tr>
<th>( v' \rightarrow v )</th>
<th>( \lambda = 0 )</th>
<th>( \lambda = 1 )</th>
<th>( \lambda = 2 )</th>
<th>( \lambda = 3 )</th>
<th>( \lambda = 4 )</th>
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<th>( \lambda = 6 )</th>
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<td>1.02850\times10^{-2}</td>
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</table>

\(a\). In this calculation, the nuclear wave functions are approximated by the Morse anharmonic wave function. The molecular constant for the \( \chi_v \)'s are those of the ground \( X_2^1 \) state of the nitrogen molecules. The molecular constant for the \( \xi_{\lambda} \)'s are taken to be \( \omega_e = 1910 \text{ cm}^{-1} \), \( x_e \omega_e = 205 \text{ cm}^{-1} \) obtained from a semiempirical calculation [Ref. 3].

\(b\). The quantity \( \xi \) is equal to \( \frac{1}{2} \omega_e (1 - \frac{1}{2} x_e) \) plus the electronic resonance energy which is taken to be 1.89 eV [obtained in Ref. 3].
FIGURE CAPTIONS

Figure 1

Energy dependence of the partial cross section for the excitation of the ground $N_2$ molecule to various excited vibrational states by electrons as observed by Schulz (Ref. 1). The circles and the crosses are the experimental data measured at the forward angle and at an angle of 72 degrees respectively. The dashed lines indicate the approximate positions of the resonance (determined by a semiempirical calculation in Ref. 3) and the solid curves are the calculated cross section using these approximate resonance positions.