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Resonant electron-molecule scattering: The impulse approximation in N_2O

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N_2O is a linear triatomic molecule. Electron scattering shows a $^2\Sigma^+$ shape resonance at ~ 2.3 eV. The lifetime turns out to be so short, 0.9×10^{-15} sec, that one has an impulse picture, in which the nuclei acquire velocity but suffer little displacement during the residence of the projectile electron. The nuclear wave equation at the resonance is solved in the impulse approximation, and is shown to give a good account of the excitation of more than 20 vibrational states observed by Azria, Wong, and Schulz.

I. INTRODUCTION

When a molecule captures an electron to form a short-lived negative ion[1] whose potential-energy surface has a local minimum sufficiently deep to prevent dissociation, the nuclei can move in different ways which depend[2] on the ratio of the vibrational period ($\equiv 2\pi/\omega$) and the decay rate ($\equiv \langle\Gamma\rangle/\hbar$).[2a] If $\omega \gg \langle\Gamma\rangle/\hbar$, one may speak of a "compound molecule" with well-defined vibrational levels; if $\omega \ll \langle\Gamma\rangle/\hbar$, one may speak of an "impulse limit"; and in the intermediate case $\omega \approx \langle\Gamma\rangle/\hbar$, one may speak of a "boomerang model." Each case has its own characteristic and easily recognizable energy dependence in the cross sections; examples of all three are listed in Refs. 2-4.

Detailed discussions of several examples of the "boomerang model" have recently been given.[4] In this paper, we discuss an example of the "impulse limit," a resonance observed[5,6] in the collision

$$e + N_2O \rightarrow N_2O(\text{vibrationally excited}) + e'$$

at an impact energy of 2.3 eV.

This paper continues the discussion of a model of molecular negative ions in which a complex energy is associated with the electronic state[7]; the imaginary part is proportional to the rate of emission of the extra electron. The complex energy is used as an adiabatic potential in a wave equation for the nuclei (see Sec. III). This model has now been used to discuss vibrational[8] and rotational[9] excitation, dissociative attachment,[10] and electron detachment[11] and associative detachment[11] in ion-molecule collisions.

We shall have to make several approximations; they will be introduced as they are needed, and are then listed again together in Sec. X.

II. STRUCTURE OF THE TRANSIENT OF N_2O^- ION

The observed cross sections in the collision $e + N_2O$ at ≈ 2.3 eV show a smooth hump without fine structure (see Figs. 1 and 2). This contrasts with a great deal of fine structure observed at some other resonances, for example, a resonance at 3.8 eV in the collision $e + CO_2$.[4] Such fine structure is a consequence of reflected components in the nuclear wave function in the negative ion, arising at the turning points in the potential-energy surface; these reflected components combine with the nuclear wave produced on capture of the incoming electron to yield an interference pattern which changes with the energy. Consequently, the amplitudes for the production of final states, which are proportional to the overlap integrals of the interference pattern with the final nuclear wave function, oscillate as a function of energy. The absence of such oscillations in the N_2O resonance at ~2.3 eV implies that there can be no significant reflected components in the nuclear wave function of the negative ion.

There are two possible reasons for the absence of the reflected components. The first possibility is that the lifetime against reemission of the extra electron is very short. (This would be the only possibility in an ion whose potential-energy surface possesses a minimum stable against dissociation into heavy fragments.) The second possibility is that the ion may dissociate into heavy fragments before reflected components can arise; this could happen in N_2O^- because the threshold for dissociative attachment, $e + N_2O \rightarrow N_2 + O^-$, lies well below the resonance energy of 2.3 eV (at 0.3 eV for a target molecule in its vibrational ground state).

To interpret the experiments, we have made the hypothesis that the first possibility holds in N_2O^-, and verified that the parameter values we need for a good fit of the observations are consistent with the hypothesis. The parameter values have to satisfy two tests: First, the autoionization rate $\Gamma(\vec{R}_0)/\hbar$ for the extra electron in the neighborhood of $\vec{R}_0$, the equilibrium configuration of the target molecule, has to be large compared with the time for a significant displacement of the nuclei [we may take this time to be of the order of $\frac{1}{4}(2\pi/\bar{\omega})$, where $\bar{\omega}$ is a typical vibrational angular frequency and

$(2\pi/\bar{\omega})$ the corresponding period]. The second test to be satisfied is a reasonable consistency of $\Gamma(\vec{R}_0)$ with the observed probability of dissociation $N_2O^- \rightarrow N_2 + O^-$, relative to the total cross section for resonant processes; this probability is given by the "survival factor," $\exp[-(1/\hbar)\int dt\,\Gamma(\vec{R}(t))]$, where t is the time reckoned from the capture of the electron and the integral has to be taken along the trajectory of dissociation. For this second test, one must of course extrapolate $\Gamma(\vec{R})$ from the value close to $\vec{R}_0$, which is all that is needed for vibrational excitation.

One reason for expecting our hypothesis to be good lies in the small magnitude, about 10^{-2}, of the observed probability for dissociative attachment ($N_2O^- \rightarrow N_2 + O^-$) relative to the sum total of all resonant processes.[12] The simplest interpretation of this factor 10^{-2} is that the N_2O^- ion dissociates rapidly (in a time of order 10^{-14} sec) as the O^- ion moves away from N_2 along the axis of the original N_2O. In this interpretation, $\Gamma(\vec{R}_0)/\hbar$ has to be so large ($\approx 10^{15}$ sec^{-1}) that the survival factor is of order 10^{-2}; most of the electron emission would then necessarily occur before the O and N_2 had moved apart significantly, in accordance with our hypothesis. An alternative, but rather implausible, interpretation of the factor 10^{-2} would have been that the small survival factor comes from a smaller value of Γ acting along a complicated trajectory which needs a time much longer than 10^{-14} sec for dissociation; this interpretation would be difficult to reconcile with the absence of oscillations in the vibrational excitation cross sections as a function of energy.

The short lifetime against autoionization gives us an example of the impulse limit, in the sense that the nuclei acquire momentum from the electrostatic force of the extra electron, but are not significantly displaced during the residence of that extra electron.

The neutral N_2O molecule is linear in its electronic ground state.[13,14] If the lifetime of the N_2O^- ion at 2.3 eV is short, we are concerned only with configurations of the nuclei close to the linear configuration of the neutral N_2O molecule. The ground state is $^1\Sigma^+$. Following Bardsley,[15] we suppose that the resonance at 2.3 eV is due to the occupation of a vacant (8σ) orbital (the number 8 means that this is the eighth one-electron σ orbital in ascending order of energy) which can be formed from atomic $2s$ and $2p$ states; thus the resonance is $^2\Sigma^+$. The form of the corresponding orbital in the isoelectronic CO_2 molecule is given in Ref. 14; the orbital has two nodal surfaces which are normal to the molecular axis where the axis passes through them. Thus the dominant partial wave to which the orbital matches in CO_2 must be a (σd) wave. In N_2O, the absence of a center of symmetry is likely to distort the orbital so as to contain a substantial (σp) wave outside the molecule in addition to the d wave.

The N_2O molecule in its electronic ground state has three normal vibrational modes[16]: a "symmetric-stretch" mode in which the two outer nuclei move apart along the molecular axis while the central nucleus almost stands still; an "asymmetric-stretch" mode, in which the central and one of the outer nuclei approach, while the third nucleus recedes from the first two along the molecular axis; and a "bending" mode, in which the nuclei move perpendicularly to the molecular axis, the central nucleus moving in the opposite direction to the other two (there are actually two degenerate bending vibrations in two perpendicular planes which contain the axis).

III. EXPRESSION FOR CROSS SECTIONS

In resonance scattering, the extra electron is trapped temporarily (together with the target electrons) in a state $\psi(q, \vec{R})$ which is localized at the molecule (the coordinates of the electrons and nuclei, respectively, are denoted by q and $\vec{R}$). The state ψ is an eigenfunction of the electronic Hamiltonian $H_{el}(q, \vec{R})$, i.e., $[H_{el} - W(\vec{R})]\psi(q, \vec{R}) = 0$, where $W(\vec{R})$ is the eigenvalue. If the extra electron moves away from the nuclei, ψ at first decreases due to the centrifugal barriers responsible for the trapping; ψ then reaches a minimum beyond which it has to match on to outgoing waves. We shall call the region inside the minimum the "inner region" (IR). In an exact theory, the outgoing waves would have to belong to the total energy in the collision. We shall use an adiabatic approximation by supposing that within the inner region, ψ may be represented by a Siegert state[17] corresponding to nu-

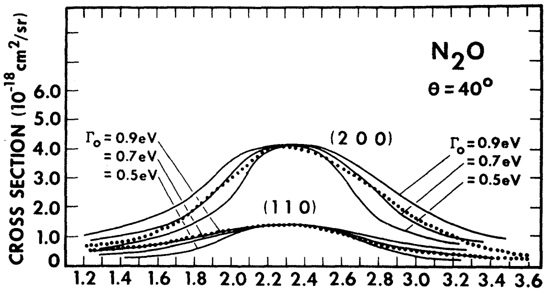

FIG. 1. Energy dependence of the differential cross sections for two different energy-loss processes. Experiment, dotted line; theory, solid line. The theoretical curves correspond to the parameters η_{SS}, η_{AS}, and B given in Sec. IX. As Γ_0 increases, so does the cross section both above and below the maximum.

clei fixed at $\vec{R}$. This implies that the outgoing waves belong to energy $W(\vec{R})$, so that the eigenvalue and the boundary condition have to be determined self-consistently. It is easily shown that as a consequence of this boundary condition, W is complex:

$$W(\vec{R}) = E(\vec{R}) - \tfrac{1}{2} i \Gamma(\vec{R}) , \tag{1}$$

where both $E(\vec{R})$ and $\Gamma(\vec{R})$ are real and $\Gamma > 0$. We shall normalize ψ so that $\int_{IR} dq\, |\psi(q, \vec{R})|^2 = 1$.

The complete wave function in the inner region is

$$\Psi(q, \vec{R}; E) = \psi(q, \vec{R}) \xi(\vec{R}; E) + \Phi_0(q, \vec{R}; E) , \tag{2}$$

where E is the total energy, ξ is the wave function of the nuclei, and Φ_0 is the nonresonant part of the wave function which contains the incoming wave. The resonance picture implies that at resonance $|\psi\xi| \gg |\Phi_0|$ in the inner region.

We shall simplify the problem by supposing that at the resonance wave distortion is adequately represented by the term $\psi\xi$; then Φ_0 may be approximated by the initial state, i.e., $\Phi_0 = \chi_0(\vec{R}) \phi_0(q, \vec{R}) \times e^{i\vec{k}_0 \cdot \vec{r}}$, where χ_0 is the initial vibrational state of the nuclei, ϕ_0 the initial electronic state of the target, and $\vec{k}_0$ the wave vector and $\vec{r}$ the position of the incident electron. Rotation of the molecule will be ignored, because the resonance lifetime $\hbar/\langle\Gamma\rangle$ is short compared with rotational periods.

To get an equation for ξ, insert Ψ into the Schrödinger equation $(H - E)\Psi = 0$. (H is the total Hamiltonian, i.e., $H = H_{el} + K$, where K is the kinetic energy of the nuclei.) Multiply by ψ^*, and integrate over the internal region to get

$$[K + W(\vec{R}) - E] \xi(\vec{R}, E) = -\zeta(\vec{R}, \vec{k}_0) \chi_0(\vec{R}) , \tag{3}$$

where

$$\zeta(\vec{R}, \vec{k}_0)\chi_0 \equiv \left(\int_{IR} dq\, \psi^*(q, \vec{R})(H - E) \times \phi_0(q, \vec{R}) e^{i\vec{k}_0 \cdot \vec{r}} \right) \chi_0 .$$

We have dropped nonadiabatic terms on the left-hand side of (3) by replacing the product $K\psi\xi$ by $\psi(K\xi)$, because the electronic wave function ψ varies much more slowly with $\vec{R}$ than does the nuclear wave function ξ. In ζ, we may replace $H - E$ by V_0, the interaction potential of the incoming electron with the target, because Φ_0 as written satisfies $[(H - V_0) - E]\Phi_0 = 0$, if we neglect nonadiabatic terms. Thus ζ is a function of $\vec{R}$, and contains no derivative operators with respect to $\vec{R}$. Therefore our approximation for Φ_0 permits formation of the ion only by tunneling through the centrifugal barriers, and not by a nonadiabatic coupling to the nuclei.

Let the final state be $\Phi_f(q, \vec{R}) = \chi_f(\vec{R}) \phi_0(q, \vec{R}) e^{i\vec{k}_f \cdot \vec{r}}$, where χ_f is the final vibrational state and $\vec{k}_f$ the wave vector of the outgoing electron. The differential cross section for the transition from Φ_0 to Φ_f is given by

$$\left(\frac{d\sigma}{d\Omega}\right)_{0\to f} = \frac{v_f}{v_0} \left(\frac{m}{2\pi\hbar^2}\right)^2 |(\Phi_f | V_f | \Psi)|^2 .$$

Here V_f is the potential between the outgoing electron and the rest of the molecule, v_0 and v_f are the velocities of the incoming and outgoing electrons, and m is the mass of the electron.

We shall retain only the resonance term $\psi\xi$ in Ψ and restrict the integration to the internal region, where the extra electron interacts with the molecule; one gets

$$\left(\frac{d\sigma}{d\Omega}\right)_{0\to f} = \frac{v_f}{v_0} \left(\frac{m}{2\pi\hbar^2}\right)^2 \left| \int' d\vec{R}\, \chi_f^*(\vec{R}) \zeta'(\vec{R}, \vec{k}_f) \xi(\vec{R}, E) \right|^2 , \tag{4}$$

where

$$\zeta'(\vec{R}, \vec{k}_f) \equiv \int_{IR} dq\, \phi_0^*(q, \vec{R}) e^{-i\vec{k}_f \cdot \vec{r}} V_f \psi(q, \vec{R}) .$$

Thus $\zeta'(\vec{R}, \vec{k}_f)$ is a function of position $\vec{R}$ only, and does not contain derivative operators with respect to $\vec{R}$. The integration in (4), and at corresponding points later, is to exclude the mass center and the orientation of the molecule; we shall distinguish all integrals over $\vec{R}$ in which the mass center and orientation are held fixed by a prime.

IV. IMPULSE APPROXIMATION

To solve Eq. (3), we shall drop the term K on the left-hand side; we call this the impulse approximation,[9,18] because it amounts to ignoring the motion of the nuclei during the short residence of the extra electron. The approximation is sometimes called the "fixed-nucleus approximation," or the "adiabatic approximation."[19]

To justify the impulse approximation, divide both sides of (3) formally by the operator $[K + W - E]$, and expand in powers of $K/(W - E)$. The impulse approximation is the leading term, $\xi = [E - W(\vec{R})]^{-1} \zeta \chi_0$. In the first-order correction term, we may ignore all derivatives except $(K\chi_0)$, because the variation of χ_0 occurs in a scale of length smaller than the scale for W and ζ by a factor of order $(m/M)^{1/4} \approx \frac{1}{10}$, where m is the electronic and M a typical nuclear mass. Since χ_0 is the vibrational ground state, $K\chi_0$ is of order $\frac{1}{4}\hbar \times \sum \omega_i \chi_0$, where ω_1 is the angular frequency of the ith vibrational mode in N_2O. On the other hand, the denominator satisfies $|W - E| \geqslant \frac{1}{2}\Gamma$, so that the correction term is smaller than the leading term by a factor of order $(\hbar \sum \omega_i)/(2\Gamma)$.

A similar criterion may be obtained by a more physical argument. The impulse approximation should be good if the lifetime of the compound state is short compared with the time of dissociation, so that most of the ions emit their extra electron before dissociation is complete. If we take the time of dissociation to be of the order of the time it takes to slide down the side of a parabolic well to the bottom, that is, of the order of $\frac{1}{4}$ of a typical vibrational period ($\equiv 2\pi/\overline{\omega}$), we must have $\hbar\overline{\omega} \ll (\frac{1}{2}\pi)\langle\Gamma\rangle$.

Within the impulse approximation, the differential cross section (4) for scattering to a vibrational state ($s'b'a'$) from an initial state (sba) becomes

$$\left(\frac{d\sigma}{d\Omega}\right)_{sba\rightarrow s'b'a'} = \frac{v_f}{v_0}\left(\frac{m}{2\pi\hbar^2}\right)^2 \left| \int' d\vec{\mathrm{R}}\, \frac{\chi^*_{s'b'a'}(\vec{\mathrm{R}})\,\zeta'(\vec{\mathrm{R}},\vec{\mathrm{k}}_f)\,\zeta(\vec{\mathrm{R}},\vec{\mathrm{k}}_0)\,\chi_{sba}(\vec{\mathrm{R}})}{E - W(\vec{\mathrm{R}})} \right|^2 . \tag{5}$$

(The notation sba signifies s quanta of symmetric stretch vibration, b quanta of bending, and a quanta of asymmetric stretch.)

V. APPROXIMATIONS IN INTEGRALS

We are concerned with scattering off the vibrational ground state, i.e., $s=b=a=0$. The Franck-Condon region defined by the initial vibrational state χ_{000} has a linear width of order $(m/M)^{1/4}a_B \simeq \frac{1}{10}a_B$, where M is a typical nuclear mass and a_B is the Bohr radius. Since the typical length in which ζ, ζ', and W vary is much larger, of order a_B, we may use linear approximations of ζ, ζ', and W as functions of the nuclear coordinates $\vec{\mathrm{R}}$. The experimental observations in Ref. 5 show that states with up to seven quanta of the symmetric-stretch vibration are excited; since the selection rules for the harmonic oscillator say that a linear term in ζ or ζ' can excite only a single vibrational quantum, the dominant mechanism for the excitation of vibrations must be the variation of $W(\vec{\mathrm{R}})$ with $\vec{\mathrm{R}}$ in the denominator of Eq. (5); we shall therefore ignore the variation of ζ and ζ' with respect to the symmetric-stretch and asymmetric-stretch distortions (and return later to discuss bending).

In the denominator, we use the linear approximation $W(\vec{\mathrm{R}}) = E_0 - \frac{1}{2}i\Gamma_0 + \sum_\alpha U_\alpha q_\alpha$, where $(E_0, \Gamma_0) = (E(\vec{\mathrm{R}}_0), \Gamma(\vec{\mathrm{R}}_0))$ corresponds to the equilibrium configuration in the electronic ground state of N_2O and q_α ($\alpha \equiv$ SS, AS) are the normal coordinates for the symmetric-stretch and asymmetric-stretch vibrations. The q_α are normalized so that the turning points of the initial vibrational state χ_{000} occur at $q_\alpha = \pm 1$. The coefficients are the slopes $U_\alpha = \partial E_0/\partial q_\alpha$, taken at $q_\alpha = 0$ for both modes in the linear configuration of the molecule. The U_α will be treated as adjustable parameters. (See Figs. 3 and 4.)

However, in the neighborhood of the linear configuration, W does not contain a term linear in ϕ, the angle between the lines which join the middle nucleus to the two outer ones. (We define the linear configuration as $\phi = 0$.) The reason lies in the Σ^+ symmetry of the resonance, which makes W vary as ϕ^2 near $\phi = 0$. Therefore, to account for the observed excitation of a single quantum of the bending vibration, we have to retain a term linear in ϕ in the product $\zeta'\zeta$ in Eq. (5).

In accordance with these arguments, we approximate the product $\zeta'\zeta$ in (5) by the expression

$$\zeta'(\vec{\mathrm{R}},\vec{\mathrm{k}}_f)\,\zeta(\vec{\mathrm{R}},\vec{\mathrm{k}}_0) \cong \overline{\zeta}'(\hat{R}_0,\hat{k}_f)\,\overline{\zeta}(\hat{R}_0,\hat{k}_0) + B\phi\,, \tag{6}$$

where $\overline{\zeta}'(\hat{R}_0\hat{k}_f) \equiv \zeta'(\vec{\mathrm{R}}_0,\vec{\mathrm{k}}_f)$, $\overline{\zeta}(\hat{R}_0,\hat{k}_0) \equiv \zeta(\vec{\mathrm{R}}_0,\vec{\mathrm{k}}_0)$; $\vec{\mathrm{R}}_0$ stands for the equilibrium position of the nuclei in the initial electronic state of N_2O, and $\hat{R}_0$ for the direction of the molecular axis. $\vec{\mathrm{k}}_f$ and $\vec{\mathrm{k}}_0$ are the outgoing and incoming wave vectors; their magnitudes correspond to the center of the resonance, and their directions are specified by $\hat{k}_f$ and $\hat{k}_0$. The quantity B is a function of $\vec{\mathrm{R}}$, $\vec{\mathrm{k}}_f$, and $\vec{\mathrm{k}}_0$; we shall eventually treat B as an adjustable parameter. The angle ϕ refers to a bending of the molecule in a particular plane defined by B; therefore only one of the two degenerate perpendicular-bending vibrations will be excited. In Sec. IX we show that our best values of the parameters make the second term in (6) smaller by a factor of 20 than the first.

VI. APPLICATION OF OPTICAL THEOREM

We next relate $\overline{\zeta}'$ and $\overline{\zeta}$ to Γ_0. The relation we obtain will be based on an argument to zero order in the displacements from the equilibrium configuration. Thus we shall be neglecting the term $B\phi$ in (6); as justification, we have the observed fact that the bending vibrations, which are excited by this term, account for only about 10% of the resonant cross section.

The two terms in Eq. (6) do not interfere in Eq. (5) because the term $B\phi$ contributes only to transitions with $b' \neq b$, while the term $\overline{\zeta}'\overline{\zeta}$ gives the transitions with $b' = b$. The part of the total cross section which arises from the term $\overline{\zeta}'\overline{\zeta}$ in (6), after averaging over the direction $\hat{R}_0$, will be denoted by σ'_T. When summing (5) over final states, one may approximate $(v_f/v_0) \cong 1$, because the ratio does not differ greatly from unity in the final states which are observed to contribute most to the total cross section.[20] By using the completeness of the final states $\chi_{s'b'a'}$, one finds

$$\sigma'_T \cong \left(\frac{m}{2\pi\hbar^2}\right)^2 4\pi\gamma^2 \int' d\vec{R}\, \frac{|\chi_{sba}(\vec{R})|^2}{|E - W(\vec{R})|^2},$$

where

$$\gamma \equiv \frac{1}{4\pi}\int d\hat{k}_f\, |\bar{\zeta}'(\hat{R}_0, \hat{k}_f)|^2 = \frac{1}{4\pi}\int d\hat{k}_0\, |\bar{\zeta}(\hat{R}_0, \hat{k}_0)|^2; \tag{7}$$

we have used the fact that averages of $|\bar{\zeta}|^2$ and $|\bar{\zeta}'|^2$ over $\hat{R}_0$ and $\hat{k}_0$ (or $\hat{k}_f$) are equivalent.

The complete total cross section will be denoted by σ_T. We obtain an expression for it from the optical theorem: $\sigma_T = (4\pi/k_0)\mathrm{Im} f(0)$, where $f(0)$ is the amplitude for elastic scattering in the forward direction. It follows that σ_T consists of distinct contributions from the resonant and direct parts of the scattering amplitude. From the expression for $f(0)$ which corresponds to Eq. (5), one obtains, with the aid of (6) and (7),

$$\sigma_T = \frac{m}{\hbar^2 k_0}\gamma\Gamma_0 \int' d\vec{R}\, \frac{|\chi_{sba}(\vec{R})|^2}{|E - W(\vec{R})|^2}. \tag{8}$$

If one equates the two expressions σ_T and σ'_T to zero order in the displacements from the equilibrium configuration in N_2O, one gets

$$\gamma = (\pi\hbar^2/mk_0)\Gamma_0. \tag{9}$$

Inserting (6), (7), and (9) into (5), one obtains finally for the partial cross sections, after averaging over the direction $\hat{R}_0$ of the molecular axis and integrating over the direction of the outgoing electron,

$$\sigma_{sba\to s'b'a'} = \frac{v_f}{v_0}\frac{\pi}{k_0^2}\Gamma_0^2 \left| \int' d\vec{R}\, \frac{\chi_{s'b'a'}(\vec{R})\chi_{sba}(\vec{R})}{E - W(\vec{R})}\right|^2 + \frac{v_f}{v_0}\left(\frac{m}{2\pi\hbar^2}\right)^2 \left(\int d\hat{k}_f \langle |B|^2\rangle\right) \left| \int d\vec{R}\, \frac{\chi_{s'b'a'}\phi\chi_{sba}}{E - W(\vec{R})}\right|^2, \tag{10}$$

where

$$\langle |B|^2\rangle \equiv (1/4\pi)\int d\hat{R}_0 |B|^2.$$

The factor ϕ in the second term has to be understood as referring to bending in one plane only.

VII. ANGULAR DISTRIBUTIONS

The observations reported in Ref. 5 were done at the single scattering angle of 40°, so that the angular distribution has to be known before a comparison can be made with the theoretical cross section integrated over all angles, given in Eq. (10).

It follows from Eqs. (5)–(7) and (9) that after an average over the direction of the molecular axis has been done, the angular distribution corresponding to the first term in (10) is given by

$$g(\hat{k}_f, \hat{k}_0) = \frac{1}{(4\pi\gamma)^2}\int d\hat{R}_0\, |\bar{\zeta}'(\hat{R}_0, \hat{k}_f)|^2 |\bar{\zeta}(\hat{R}_0, \hat{k}_0)|^2.$$

The normalization has been chosen so that $\int d\hat{k}_f \times g(\hat{k}_f, \hat{k}_0) = 1$, so that the differential cross section corresponding to the first term in (10) is obtained by multiplying by the factor $g(\hat{k}_f, \hat{k}_0)$.

As we have already mentioned in Sec. II, the dominant partial waves appearing in $\bar{\zeta}(\hat{R}_0, \hat{k}_0)$ and $\bar{\zeta}(\hat{R}_0, \hat{k}_f)$ should be σd and σp. The corresponding forms on the function g are (with θ the angle between $\hat{k}_0$ and $\hat{k}_f$)

$$(\sigma p):\quad g(\hat{k}_f, \hat{k}_0) = (1/4\pi)\tfrac{3}{5}(1 + 2\cos^2\theta),$$

$$g(40°) = 1.3/4\pi$$

$$(\sigma d):\quad g(\hat{k}_f, \hat{k}_0) = (1/4\pi)\tfrac{15}{14}(1 - 2\cos^2\theta + 3\cos^4\theta),$$

$$g(40°) = 0.92/4\pi.$$

We have not attempted to obtain an angular distribution corresponding to the second term in (10), which accounts for the excitation of the bending vibration; we shall treat $\langle |B|^2\rangle$ at 40° as a parameter.

The expression for the differential cross sections which has to be compared with experiment is now, from (10),

$$\left(\frac{d\sigma}{d\Omega}\right)_{sba\to s'b'a'} = \frac{v_f}{v_0}\frac{\pi}{k_0^2}\Gamma_0^2 g(\hat{k}_f, \hat{k}_0) \times \left| \int' d\vec{R}\, \frac{\chi^*_{s'b'a'}(\vec{R})\chi_{sba}(\vec{R})}{E - W(\vec{R})}\right|^2 + \frac{v_f}{v_0}\left(\frac{m}{2\pi\hbar^2}\right)^2 \langle |B|^2\rangle(\hat{k}_f, \hat{k}_0) \times \left| \int' d\vec{R}\, \frac{\chi^*_{s'b'a'}(\vec{R})\phi\chi_{sba}}{E - W(\vec{R})}\right|^2. \tag{11}$$

VIII. EVALUATION OF INTEGRALS

The integrals in Eqs. (8) and (10) have to be evaluated. It is convenient to factorize $\chi_{sba} = \mu_s(q_{SS})\beta_b(\phi)\alpha_a(q_{AS})$, the three factors being nuclear vibrational states for the symmetric-stretch, bending, and asymmetric-stretch modes. [There should, strictly speaking, be two factors for bending, but since only one is affected by the factor ϕ in Eq. (10), the other can be taken to the ground state, which contributes a factor 1 to all integrals.]

The factors $\mu_s\alpha_a$, and the associated integrations over q_{SS} and q_{AS}, contribute to both integrals in Eq. (10) a factor[21]

$$I_{s'a',\,sa} \equiv \int dq_{\rm SS}\, dq_{\rm AS}\, \frac{\mu^*_{s'}(q_{\rm SS})\,\alpha^*_{a'}(q_{\rm AS})\,\mu_s(q_{\rm SS})\,\alpha_a(q_{\rm AS})}{E - W(\vec{\rm R})}\,.$$

This integral may be evaluated if one writes

$$\frac{1}{E - W(\vec{\rm R})} = (-i)\int_0^\infty d\omega\, e^{i\omega[E - W(\vec{\rm R})]}$$

(convergence being guaranteed by the condition $\Gamma > 0$), and uses the generating functions for the states of the harmonic oscillator to represent the factors μ and α. In the special case $s = a = 0$, Appendix A with the linear approximation for W gives

$$I_{s'a',\,00} = \left(\frac{-2i}{\Gamma_0}\right)\frac{(-i\eta_{\rm SS})^{s'}(-i\eta_{\rm AS})^{a'}}{(s'!\,a'!)^{1/2}2^{(s'+a')/2}} \times \int_0^\infty d\omega\, \omega^{s'+a'} \exp[-(\omega - i\omega e + A\omega^2)]\,, \tag{12}$$

where

$$A \equiv \tfrac{1}{4}(\eta^2_{\rm SS} + \eta^2_{\rm AS})\,,$$

$$\eta_{\rm SS} \equiv 2U_{\rm SS}/\Gamma_0\,, \quad \eta_{\rm AS} \equiv 2U_{\rm AS}/\Gamma_0\,,$$

$$\epsilon \equiv (E - E_0)/\tfrac{1}{2}\Gamma_0\,.$$

Since $2U_{\rm SS}$ and $2U_{\rm AS}$ are the Franck-Condon (FC) widths with respect to symmetric and asymmetric stretch distortion, $\eta_{\rm SS}$ and $\eta_{\rm AS}$ are the ratios of the FC width to the decay width. The integral in Eq. (12) has to be evaluated numerically.

In the results given in Sec. IX, we have confined ourselves to fitting the observations at a scattering angle at 40°; the formula (8) for σ_T has been used only to derive Eq. (9) above. Nevertheless, for the sake of completeness, we shall discuss the integral in Eq. (8). The integral may be evaluated with the aid of the transformation

$$|E - W(\vec{\rm R})|^{-2} = \int_0^\infty dx \exp[-x\,|E - W(\vec{\rm R})|^2]$$

(see Appendix B). For the case $s = a = 0$, and at the center of the resonance ($E = E_0$), Appendix B shows that the coordinates $q_{\rm SS}$ and $q_{\rm AS}$ contribute a factor

$$\int_{-\infty}^{\infty} dq_{\rm SS}\, dq_{\rm AS}\, \frac{|\mu_0(q_{\rm SS})|^2\,|\alpha_0(q_{\rm AS})|^2}{|E - W(\vec{\rm R})|^2} = \left(\frac{2}{\Gamma_0}\right)^2 \int_0^\infty dx\, \frac{e^{-x}}{(1 + 4Ax)^{1/2}}\,;$$

the bending coordinates contribute a factor unity. Thus Eq. (8) becomes, with the aid of (9),

$$\sigma_T = \frac{4\pi}{k_0^2}\int_0^\infty dx\, \frac{e^{-x}}{(1 + Ax)^{1/2}} \quad \text{at } E = E_0\,. \tag{13}$$

Expression (13) decreases monotonically as A increases from zero. The limiting forms of the integral given in Appendix B, Eqs. (B7) and (B8), lead to

$$\sigma_T = \frac{4\pi}{k_0^2}[1 - 2A + O(A^2)] \quad (A \ll 1;\ \ E = E_0)\,, \tag{13a}$$

$$\sigma_T = \frac{4\pi}{k_0^2}\left(\frac{\pi}{4}\right)^{1/2}\frac{\Gamma_0}{(U^2_{\rm SS} + U^2_{\rm AS})^{1/2}} \times \left(1 - \frac{1}{\sqrt{\pi}}A^{-1/2} + \frac{1}{12\sqrt{\pi}}A^{-3/2} + \cdots\right). \quad (A \gg 1;\ \ E = E_0)\,. \tag{13b}$$

The dependence on A has a simple interpretation. In (13a), the Franck-Condon width is so small that the resonant cross section approaches the result corresponding to fixed nuclei. In (13b), the intrinsic width Γ_0 is small compared with the Franck-Condon width $(U^2_{\rm SS} + U^2_{\rm AS})^{1/2}$, which combines the effect of the vibrational coordinates; the formula (13b) tells us that even if $E = E_0$, the incoming electron is in resonance with the molecule only over a fraction $(\frac{1}{4}\pi)^{1/2}\Gamma_0/(U^2_{\rm SS} + U^2_{\rm AS})^{1/2}$ of the vibrational sweep.

IX. RESULTS

Formula (11) contains five parameters, Γ_0, $g(40°)$, $U_{\rm SS}$, $U_{\rm AS}$, and $\langle|B^2|\rangle(40°)$. They have to be adjusted to fit the magnitude and energy dependence of the cross sections to 20 different final channels.

There should be some direct contribution to the excitation of the lower states, since all three vibrational modes are optically allowed in N_2O. We have estimated the direct contribution by calculating the differential excitation cross sections at 40° in the Born approximation.[22] The results are shown in Table I. Consequently we have omitted the point (001) from the fitting procedure.

There is a variety of ratios of cross sections by which the theory can be tested in a way which is completely independent of the values of the parameters. Figure 5 is an example; it shows the ratio

$$(s' + 1)\frac{(d\sigma/d\Omega)_{000\to s'+1\,00}}{(d\sigma/d\Omega)_{000\to s'01}}$$

at 40°, which should be a constant. [The value of the constant is $(U_{\rm SS}/U_{\rm AS})^2$.]

With the value of this ratio, it is now easy to

TABLE I. Differential excitation cross sections at 40°.

	Born approximation	Experiments
(1 0 0)	12.6×10^{-19} cm^2/sr	96×10^{-19} cm^2/sr
(0 1 0)	4.2	45
(0 0 1)	43.4	28

determine the parameters needed to produce the fit shown in Figs. 1 and 2. The best values are $\Gamma_0=0.7$ eV, $U_{SS}=0.84$ eV, $U_{AS}=0.39$ eV, $g(40°)=1.2/4\pi$, $\langle|B^2|\rangle(40°)=0.011$ a.u. For the parameter A in Sec. VII, we obtain the value 1.72 (from Γ_0, U_{SS}, and U_{AS}). The lifetime corresponding to Γ_0 is $\hbar/\Gamma_0=0.9\times10^{-15}$ sec.

There are some restrictions on the values which are acceptable.

(i) The value of $g(40°)$ should lie somewhere between the values $1.3/4\pi$ and $0.92/4\pi$ given in Sec. VII, for pure σp and σd waves.

(ii) U_{SS} should be of the order of the value 0.76 eV calculated by Claydon *et al.*[13] in the isoelectronic molecule CO_2.

(iii) One expects U_{AS} to be smaller than U_{SS} because in the isoelectronic CO_2 the existence of a center of symmetry forces U_{AS} to vanish.

(iv) The parameters must take the second term in Eq. (6) small compared with the first. From the zero-point vibrational amplitude we estimate a root-mean square value of 0.1 rad for ϕ in the ground state of the molecule. From Eq. (7), we have $\bar{\zeta}'\bar{\zeta}\approx\gamma$; from (9) and the value of Γ_0, we obtain $\gamma\approx0.2$; our best values demand $|B|\approx10^{-1}$. Thus the first term on the right-hand side of (6) is of order 0.2 (in a.u.), and the second term is of order 10^{-2}, i.e., smaller by a factor 20.

X. LIST OF APPROXIMATIONS

Since a number of approximations have been introduced at convenient but separate points, we now list them together.

(a) In Eq. (2), the complete wave function Ψ was approximated by the sum of the incident plane wave and a product of a Siegert state ψ and a nuclear wave function ξ to represent the resonance. The Siegert state ψ was used only in the internal region, by cutting off all integrals in which it appeared at the boundary of the internal region.

(b) Nonadiabatic terms were dropped to obtain Eq. (3) for the nuclear wave function ξ.

(c) Only the resonant part $\psi\xi$ of Ψ was used in calculating the cross sections [see Eq. (4)]. Potential scattering was ignored.

(d) Equation (3) for ξ was solved in the impulse approximation, by dropping the nuclear kinetic energy K (see Sec. IV). This approximation would not be justified in a case where substantial displacement of the nuclei occurs during the residence of the extra electron, as in the boomerang model[4] or in the compound molecule.[3]

(e) The complex potential $W(\vec{R})$ and the entry and emission amplitudes ξ, ζ, and ζ' were expanded in powers of the displacements of the nuclei with respect to the normal modes of the target molecule; we consistently retained only the lowest-order terms which would lead to the observed excitations (see Sec. V).

(f) To obtain the relation (9) between the entry and exit amplitudes and the total decay width, we equated the expressions for the total cross section from the optical theorem and from summing the partial cross sections; only resonant terms were retained in each case, and only the terms of zero order in the displacements from the equilibrium configuration of N_2O in its ground state.

(g) The velocity factors (v_f/v_0) were set equal to one in the calculations of the total cross section which led to Eq. (9).

(h) The five quantities listed in the first line of Sec. IX were treated as adjustable parameters.

We conclude from Figs. 1–5 that with these approximations the impulse approximation gives a good and self-consistent account of the observed excitations. The values attached to the parameters for the best fit are reasonable.

XI. DISCUSSION

The agreement between experiment and theory shown in Figs. 1 and 2 is satisfactory for the states ($s'00$) and ($s'01$). For the excitation of states ($s'02$), and the higher members of the sequence ($s'10$), which are accidentally degenerate within the experimental energy resolution, the

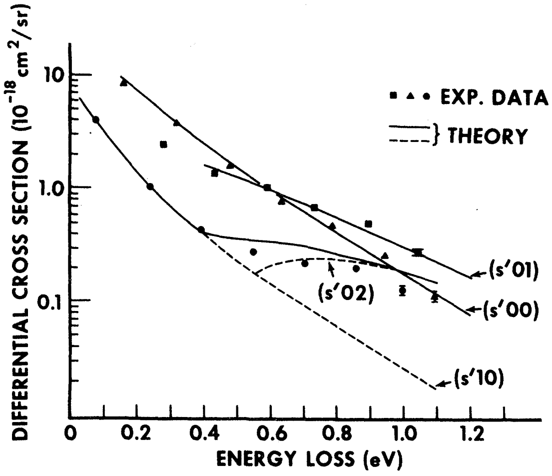

FIG. 2. Magnitude of differential vibrational cross sections at 40° vs energy loss. Experiment: ■, ▲, ●; theory: solid line. The notation $s'b'a'$ is explained at the end of Sec. IV. For the sake of clarity, the theoretical points have been joined by continuous curves. The excitations ($s'02$) and ($s'10$) are accidentally degenerate within the experimental resolution for energy losses exceeding 0.4 eV; the broken curves are the calculated cross sections for these two excitations separately. The sum of these broken curves is shown as a continuous curve above 0.4 eV.

summed cross sections from the theory are too large by about 50%, although the relative magnitudes agree well with experiment.

In Fig. 2 the maximum in the calculated curve joining the points ($s'02$), and also the reduction in slope as one goes from ($s'00$) to ($s'01$), are both consequences of the impulse picture. The potential-energy surface $E(\vec{R})$ in the N_2O^- ion has well-defined slopes in both the symmetric-stretch and asymmetric-stretch directions; the impulse is delievered to nuclei points along the resultant slope. Therefore an excitation corresponding to a large component of impulse in the AS direction must also have a large component of impulse in the SS direction.

The value obtained for Γ_0 from the best fit, 0.7 eV, is reasonable in relation to our criterion $\frac{1}{2}\pi\Gamma_0 \gg \hbar\bar{\omega}$, which was given in Sec. IV as determining whether the impulse approximation is valid. $\bar{\omega}$ was the angular frequency of vibration in a parabolic potential well such that the slide from a point on the side to the bottom should take a time of the order the N_2O^- ion takes to dissociate. We get $\frac{1}{2}\pi\Gamma_0 = 1.0$ eV, and that is substantially larger than any reasonable value one could consider for $\hbar\bar{\omega}$. Therefore Γ_0 satisfies the first test mentioned in Sec. II.

To check that our value of Γ_0 is consistent with the observed probability of dissociative attachment, we estimated the "survival factor" (see Sec. II) in the way described in Appendix C. The value

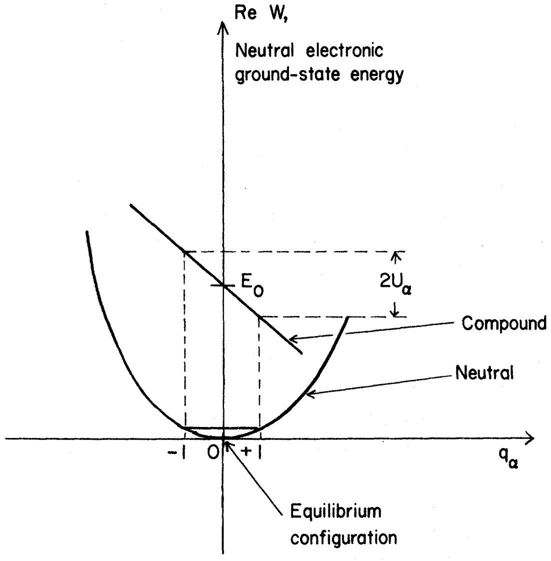

FIG. 3. Meaning of U_α. The curves show cuts through the potential-energy surfaces along the axis for the normal vibrational coordinate q_α in the neutral molecule. The parabolic curve belongs to the neutral molecule; the line sloping down to the right is the linear approximation to the real part of the complex electronic energy in the negative ion. U_α is one-half the vertical drop along the linear approximation for ReW between the turning points of the initial vibrational state in the neutral molecule. The normal coordinate q_α is scaled so that the turning points correspond to $q_\alpha = \pm 1$. The "Franck-Condon width" is $2U_\alpha$.

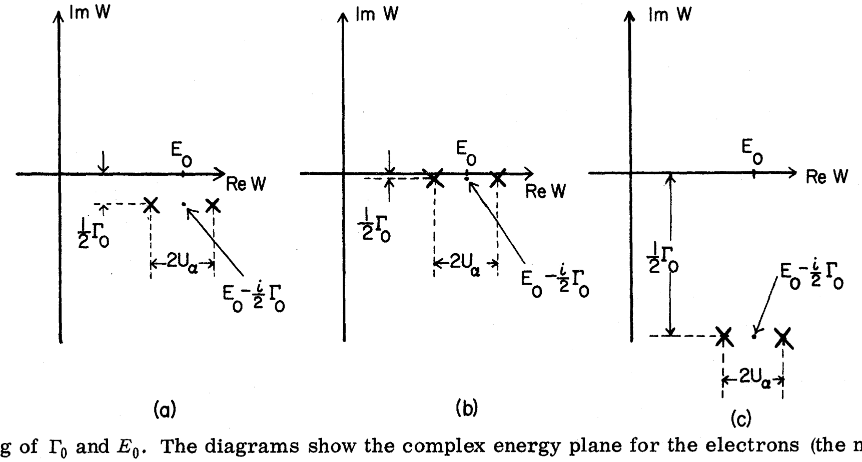

FIG. 4. Meaning of Γ_0 and E_0. The diagrams show the complex energy plane for the electrons (the nuclei are regarded as fixed). The origin corresponds to the neutral molecule, with the nuclei in their equilibrium configuration in the electronic ground state, plus an extra electron at rest at infinity. The compound-state energy corresponding to the equilibrium configuration in the neutral state is $W(\vec{R}_0) = E_0 - (i/2)\Gamma_0$. The two crosses at $q_\alpha = \pm 1$ give W corresponding to configurations displaced from the ground-state equilibrium in the neutral; except for the shift in the coordinate q_α, the configuration is unchanged from the equilibrium. Because of our approximation $\Gamma = \Gamma_0 \equiv \Gamma(\vec{R}_0)$, the two crosses are at the same distance from the real axis. The interval between the points $q_\alpha = \pm 1$ is $2U_\alpha$, the "Franck-Condon width," according to Fig. 3. The three cases (a), (b), and (c) illustrate different possible relations between $2U_\alpha$ and Γ. The compound state of N_2O^- treated in this paper is like case (a) for the asymmetric stretch, and between cases (a) and (b) for the symmetric stretch. (According to the fit quoted in Sec. IX, $U_{AS}/\frac{1}{2}\Gamma_0 = 1.1$, $U_{SS}/\frac{1}{2}\Gamma_0 = 2.4$.) (a) $\frac{1}{2}\Gamma_0 \approx U_\alpha$; (b) $\frac{1}{2}\Gamma_0 \ll U_\alpha$; (c) $\frac{1}{2}\Gamma_0 \gg U_\alpha$.

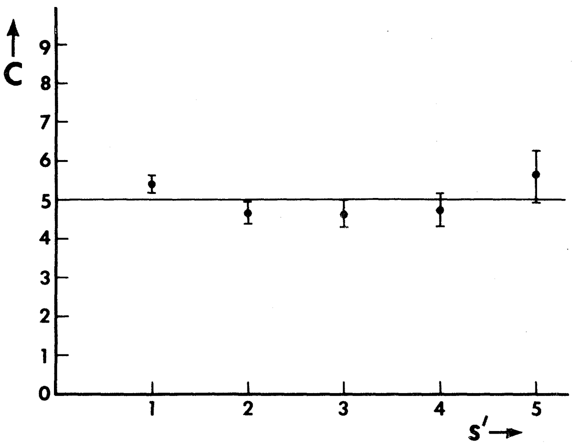

FIG. 5. Ratio of differential cross sections:

$$C \equiv (s'+1)\frac{(d\sigma/d\Omega)_{\underrightarrow{000}\, s'+1\ 00}}{(d\sigma/d\Omega)_{\underrightarrow{000}\, s'01}}.$$

This ratio of experimental cross sections should be constant if the impulse approximation is valid, irrespective of the values of the parameters. The cross bars correspond to the probable errors of measurement; the solid horizontal line is the mean of the experimental points.

depends critically on the O^--N_2 separation at the point of stabilization against autoionization. If we take the distance of this point from the N_2O equilibrium configuration to be equal to the value given for OC-O^- in Ref. 13, we get a survival factor of about 10^{-2}; this agrees with the observed value mentioned in Sec. II.

The present results have added an example to the list which has previously demonstrated the power of the complex-potential model for molecular negative ions, based on Eq. (3), in vibrational excitation, rotational excitation, dissociative attachment, and electron detachment (see Refs. 1–4 and 10 and 11).

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APPENDIX A: DERIVATION OF EXPRESSION (12) FOR INTEGRAL $I_{s'a'00}$

In Sec. VIII, we defined the integral

$$I_{s'a',sa} \equiv \int dq_{SS}\, dq_{AS}\, \frac{\mu^*_{s'}(q_{SS})\,\alpha^*_{a'}(q_{AS})\,\mu_s(q_{SS})\,\alpha_a(q_{AS})}{E - W(\vec{R})}. \tag{A1}$$

The harmonic oscillator wave functions μ and α have the form

$$\mu_{s'}(q_{SS}) = N_{s'}H_{s'}(q_{SS})e^{-(1/2)q^2_{SS}},$$

$$\alpha_{a'}(q_{AS}) = N_{a'}H_{a'}(q_{AS})e^{-(1/2)q^2_{AS}},$$

where $H_n(q)$ is the nth-degree Hermite polynomial and where the normalization constants are

$$N_{s'} = \left(\frac{1}{\pi^{1/2}2^{s'}s'!}\right)^{1/2}, \quad N_{a'} = \left(\frac{1}{\pi^{1/2}2^{a'}a'!}\right)^{1/2}. \tag{A2}$$

With this normalization one obtains, if one drops the factor $(E-W)^{-1}$ from $I_{s'a',sa}$,

$$\int dq_{SS}\, dq_{AS}\, \mu^*_{s'}(q_{SS})\,\alpha^*_{a'}(q_{AS})\,\mu_s(q_{SS})\,\alpha_a(q_{AS}) = \delta_{s's}\delta_{a'a},$$

in accordance with the Ref. 21.

It is convenient to use the integral representation

$$\frac{1}{E-W(\vec{R})} = (-i)\int_0^\infty d\omega\, e^{i\omega[E-W(\vec{R})]},$$

with the approximation

$$E - W(\vec{R}) = E - (E_0 - \tfrac{1}{2}i\Gamma_0 + U_{SS}q_{SS} + U_{AS}q_{AS})$$

$$= \tfrac{1}{2}\Gamma_0(\epsilon + i - \eta_{SS}q_{SS} - \eta_{AS}q_{AS}),$$

where

$$\epsilon \equiv 2(E-E_0)/\Gamma_0, \quad \eta_{SS} \equiv 2U_{SS}/\Gamma_0, \quad \eta_{AS} = 2U_{AS}/\Gamma_0.$$

Expression (A1) now becomes, in the special case $s = a = 0$,

$$I_{s'a',00} = \left(-\frac{2i}{\Gamma_0}\right)\int_0^\infty d\omega\, e^{-(\omega - i\omega\epsilon)}$$

$$\times \int_{-\infty}^{\infty} dq_{SS}\, N_{s'}N_0 H^*_{s'}(q_{SS})H_0(q_{SS})e^{-q^2_{SS} - i\omega\eta_{SS}q_{SS}}$$

$$\times \int_{-\infty}^{\infty} dq_{AS}\, N_{a'}N_0 H^*_{a'}(q_{AS})H_0(q_{AS})e^{-q^2_{AS} - i\omega\eta_{AS}q_{AS}}. \tag{A3}$$

To evaluate the integrals over q_{SS} and q_{AS}, we use the generating function

$$e^{-p^2+2p\xi} = \sum_{n=0}^{\infty}\frac{H_n(\xi)}{n!}p^n.$$

Thus

$$\int_{-\infty}^{\infty} dq_{SS}\, e^{-p^2+2pq_{SS}}e^{-q^2_{SS} - i\omega q_{SS}\eta_{SS}}$$

$$= \sum_{s'=0}^{\infty}\frac{p^{s'}}{s'!}\int_{-\infty}^{\infty} dq_{SS}\, H^*_{s'}(q_{SS})H_0(q_{SS})e^{-q^2_{SS} - i\omega\eta_{SS}q_{SS}}. \tag{A4}$$

Since

$$-p^2 + 2pq_{SS} - q^2_{SS} - iq_{SS}\eta_{SS}$$

$$= -[q_{SS} - (p - \tfrac{1}{2}i\omega\eta_{SS})]^2 - i\eta_{SS}p\omega - \tfrac{1}{4}\omega^2\eta^2_{SS},$$

the integral on the left-hand side of (A4) becomes

$$\exp(-i\eta_{SS}p\omega+\tfrac{1}{4}\omega^2\eta_{SS}^2)\int_{-\infty}^{\infty}dq_{SS}\exp\{-[q_{SS}-(p-\tfrac{1}{2}i\omega\eta_{SS})]^2\}$$
$$=\sqrt{\pi}\exp(-i\eta_{SS}p\omega+\tfrac{1}{4}\omega^2\eta_{SS}^2)\,.$$

If one expands in powers of p, and equates the coefficient of $p^{s'}$ on both sides of (A4) one obtains

$$\int_{-\infty}^{\infty}dq_{SS}H_{s'}^*(q_{SS})H_0(q_{SS})e^{-q_{SS}^2-i\omega\eta_{SS}q_{SS}}$$
$$=\pi^{1/2}\omega^{s'}(-i\eta_{SS})^{s'}\exp(-\tfrac{1}{4}\omega^2\eta_{SS}^2)\,. \quad (A5)$$

A similar result holds for the coordinate q_{AS}.

Inserting (A2) and (A5) into (A3), one finds

$$I_{s'a',00}=\left(-\frac{2i}{\Gamma_0}\right)\frac{(-i\eta_{SS})^{s'}(-i\eta_{AS})^{a'}}{(s'!a'!)^{1/2}2^{(s'+a'/2)}}$$
$$\times\int_0^{\infty}d\omega\,\omega^{s'+a'}e^{-(\omega-i\omega\epsilon+A\omega^2)}\,,$$

where

$$A=\tfrac{1}{4}(\eta_{SS}^2+\eta_{AS}^2)\,. \quad (A6)$$

APPENDIX B: DERIVATION OF EQ. (13)

When the integral

$$\int' d\vec{R}\,\frac{|\chi_{sba}(\vec{R})|^2}{|E-W(\vec{R})|^2}$$

in Eq. (8) is expressed in normal coordinates for the special case $s=a=0$, the coordinates q_{SS} and q_{AS} contribute a factor

$$I=\int dq_{SS}\,dq_{AS}\,\frac{|\mu_0(q_{SS})|^2|\alpha_0(q_{AS})|^2}{|E-W(\vec{R})|^2}\,, \quad (B1)$$

where

$$\mu_0(q_{SS})=\pi^{-1/4}e^{-(1/2)q_{SS}^2}\,,$$
$$\alpha_0(q_{SS})=\pi^{-1/4}e^{-(1/2)q_{AS}^2}\,.$$

As we remarked in Ref. 21, the normalization of I is determined by the requirement that I must become equal to unity if the factor $|E-W|^{-2}$ is dropped.

It is convenient to use the representation

$$\frac{1}{|E-W(\vec{R})|^2}=\int_0^{\infty}dx\exp[-x|E-W(\vec{R})|^2]\,. \quad (B2)$$

We use the linear approximation

$$E-W(\vec{R})=\tfrac{1}{2}\Gamma_0(\epsilon+i-\eta_{SS}q_{SS}-\eta_{AS}q_{AS})\,, \quad (B3)$$

which we have already used to derive Eq. (A3) in Appendix A. At the center of the resonance, we have $\epsilon=0$, so that

$$I(\epsilon=0)=\left(\frac{2}{\Gamma_0}\right)^2\frac{1}{\pi}\int_0^{\infty}dx\,e^{-x}\int_{-\infty}^{\infty}dq_{SS}$$
$$\times\int_{-\infty}^{\infty}dq_{AS}\exp\left(-\sum_{(i,j)=(SS,AS)}B_{ij}q_iq_j\right)\,,$$

where

$$\sum_{ij}B_{ij}q_iq_j\equiv(1+x\eta_{SS}^2)q_{SS}^2+(1+x\eta_{AS}^2)q_{AS}^2$$
$$+2x\eta_{SS}\eta_{AS}q_{SS}q_{AS}\,. \quad (B4)$$

We may use the formula[23]

$$\left(\prod_{t=1}^{n}\int_{-\infty}^{\infty}dq_t\right)\exp\left(-\sum_{u,v=1}^{n}B_{uv}q_uq_v\right)=\frac{\pi^{n/2}}{(\det B)^{1/2}}\,. \quad (B5)$$

In the present case, $\det B=1+4Ax$, where $A=\tfrac{1}{4}(\eta_{SS}^2+\eta_{AS}^2)$. One obtains, from (B4),

$$I(\epsilon=0)=\left(\frac{2}{\Gamma_0}\right)^2\int_0^{\infty}dx\,\frac{e^{-x}}{(1+4Ax)^{1/2}}\,. \quad (B6)$$

A limiting form for I valid when $A\ll1$ follows if one expands in powers of A under the integral sign. The leading terms are

$$\frac{I(\epsilon=0)}{(2/\Gamma_0)^2}=\int_0^{\infty}dx\,\frac{e^{-x}}{(1+4Ax)^{1/2}}$$
$$=[1-2A+O(A^2)]\quad\text{for } A\ll1\,. \quad (B7)$$

If $A\gg1$, one gets an expansion in powers of A^{-1} by changing the integration variable to $y=x+\tfrac{1}{4}A$. Then

$$I(\epsilon=0)=\left(\frac{2}{\Gamma_0}\right)^2\frac{e^{1/4A}}{2A^{1/2}}\int_{1/4A}^{\infty}dy\frac{e^{-y}}{\sqrt{y}}$$
$$=\left(\frac{2}{\Gamma_0}\right)^2\frac{e^{1/4A}}{2A^{1/2}}\left(\int_0^{\infty}dy\frac{e^{-y}}{\sqrt{y}}-\int_0^{1/4A}dy\frac{e^{-y}}{\sqrt{y}}\right)\,.$$

The first integral in the parentheses $(\cdots)$ is $\sqrt{\pi}$. The second becomes, when $A\gg1$,

$$\int_0^{1/4A}dy\frac{e^{-y}}{\sqrt{y}}=\int_0^{1/4A}dy\,y^{-1/2}(1-y+\tfrac{1}{2}y^2+\cdots)$$
$$=A^{-1/2}-\tfrac{1}{12}A^{-3/2}+\cdots\,.$$

Thus when $A\gg1$,

$$\frac{I(\epsilon=0)}{(2/\Gamma_0)^2}=\int_0^{\infty}dx\,\frac{e^{-x}}{(1+4Ax)^{1/2}}$$
$$=\frac{e^{1/4A}}{2A^{1/2}}(\sqrt{\pi}-A^{-1/2}+\tfrac{1}{12}A^{-3/2}+\cdots)\,. \quad (B8)$$

APPENDIX C: PROBABILITY FOR DISSOCIATIVE ATTACHMENT

To check that our value of Γ_0 is consistent with the observed probability for the decay $N_2O^-\rightarrow N_2+O^-$ (i.e., satisfies the second test mentioned in Sec. II), we have estimated the survival factor $\exp[-(1/\hbar)\int dt\,\Gamma(\vec{R}(t))]$ (see Sec. II). The potential energy $E(R)$ for the N_2O^- ion and the potential energy in the electronic ground state of N_2O were both approximated by straight lines as functions of the displacement of the O nucleus with respect to the N_2 fragment. The two straight lines were fixed by the resonance energy of 2.3 eV in the equilibrium configuration of N_2O, and by the observed dissociation energy $N_2O \rightarrow N_2 + O(^1D)$ and $N_2O^- \rightarrow N_2 + O^-(^2P)$ at a certain displacement R_D of the O-N_2 distance from its equilibrium value in N_2O.

The displacement R_S, at which the straight lines representing the potential energies of N_2O^- and N_2O cross, has been treated as an adjustable parameter to reproduce the observed survival factor. As a function of the N_2-O^- displacement R, the electronic width was approximated by the expression.[24]

$$\Gamma(\vec{R}) = \Gamma_0 \frac{k(\vec{R})}{k_0} \frac{v_1(k(\vec{R})R_M)}{v_1(k_0 R_M)} .$$

Here $[\hbar^2 k^2(\vec{R})]/2m$ is the energy of emission of the extra electron at $\vec{R}$ and R_M is the radius of the molecule which we took to be $R_M = 1.6$ Å from the value of the van der Waals b coefficient for N_2O. The factors v_1 are the expressions for the penetrabilities of the centrifugal barrier given in Ref. 24.

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[13] Electronic energies have been calculated for the isoelectric molecule CO_2 by C. R. Claydon, G. A. Segal, and H. S. Taylor [J. Chem. Phys. 52, 3387 (1970)].

[14] A correlation diagram for the molecular orbitals is given by G. Herzberg, [*Electronic Spectra of Polyatomic Molecules* (Van Nostrand, New York, 1966), p. 314]. A corresponding calculated order of molecular orbitals in CO_2 is given in Ref. 13 (see also Table 37 on p. 345 of Herzberg's book). We have supposed the order of orbital energies in N_2O to be as in CO_2 in Ref. 13, Fig. 1.

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[21] The normalization of the integrals in (8), (10), and (11), when expressed in normal coordinates, may be obtained by omitting the factor $|E-W|^{-2}$ in (8), the factor $(E-W)^{-1}$ in the first integral in (10) and (11), and the factor $\phi(E-W)^{-1}$ from the second integral in (10) and (11). From the integral in (8) one gets $\int' d\vec{\mathrm{R}}|\chi_{sba}(\vec{\mathrm{R}})|^2=1$. From the integrals in (10) and (11), one obtains $\int' d\vec{\mathrm{R}}\, \chi_{s'b'a'}(\vec{\mathrm{R}})\chi_{sba}(\vec{\mathrm{R}})=\delta_{s's}\delta_{b'b}\delta_{a'a}$.

[22] The matrix element for the excitation of an optically allowed state in the Born approximation contains the radial coordinate of the projectile electron in a factor $\int_0^\infty dr\, r^2 j_1(qr)V(r)$, where $V(r)$ is the radial dependence of the transition potential, q the momentum change in the collision, and j_1 the spherical Bessel function of order one. Outside the molecule, one has $V(r)\propto r^{-2}$; inside, $V(r)\propto r$, approximately. At an electron energy of 2.3 eV, and a scattering angle of 40°, one has $q\cong 0.30a_B^{-1}$. Therefore, the first maximum of $j_1(qr)$ occurs at $r=2.2q^{-1}\cong 7a_B$, which is well outside the molecule. If follows that within the molecule the integrand is small, behaving like r^4. Outside the molecule, the integrand behaves like $j_1(qr)$, with a maximum at $r\cong 3.5$ Å. Most of the integral therefore comes from well outside the molecule, where the distortion of the incoming and outgoing states of the projectile is small. Therefore the Born approximation should be adequate for a rough estimate of the direct excitation even at low energies.

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