Vibrational excitation in N_2O via the 2.3-eV shape resonance*

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The vibrational excitation of N₂O by electrons in the energy range 1-4 eV has been studied with a crossed-beam apparatus using an energy resolution of 22 meV and an observation angle of 40°. The scattering in the middle of this energy range is dominated by the ${}^{2}\Sigma^{+}$ shape resonance which contributes to the excitation of about 20 vibrational modes. The vibrational modes belong to four series, namely, the n 00, n 10, n 01, and n 02 series with the quantum number n ranging from 0 to 7. The energy dependence of the differential vibrational cross sections is bell shaped and exhibits no fine structure. At the center of the ${}^{2}\Sigma^{+}$ resonance (2.3 eV), the n 00 series is most intensely excited and has a cross section of $(9.6 \pm 3.5) \times 10^{-18}$ cm²/sr for n = 1 and an exponentially decreasing magnitude for successively higher n. A similar trend of the branching ratio has also been observed in the n01 series. The present experiment combined with a calculation of Dubé and Herzenberg demonstrates that the impulse picture which was originally proposed for the case of vibrational and rotational excitation in H₂, is applicable to this triatomic molecule as well. The width Γ for the ${}^{2}\Sigma^{+}$ shape resonance of N₂O has been found to be 0.7 eV in the center of the Franck-Condon region, and it decreases for larger internuclear separations.

I. INTRODUCTION

Vibrational excitation by electron impact via shape resonances is a process well understood for diatomic molecules.¹⁻³ The lifetime of these resonances influences (i) the features displayed in the energy dependence of the vibrational excitation cross sections and (ii) the relationship of the magnitudes of cross sections to successive vibrational levels. With the exception of CO_2 , 4^{-7} vibra *tional excitation* by electron impact on polyatomic molecules is not well understood. However, the locations of low-lying shape resonances in many polyatomic systems (e.g., NO₂, N₂O, C₆H₆, H₂S, $C_{2}H_{4}$) have been measured by transmission⁸ and dissociative attachment experiments. In the particular case of N_2O , which is a linear asymmetrical molecule, a shape resonance is centered^{9,10} around 2.3 eV. This second resonance of N₂O⁻ has a configuration¹⁰

 $^{2}\Sigma^{+}[K](1\pi)^{4}(2\pi)^{4}(8\sigma)$.

In this paper, which is a continuation of the work of Boness and Schulz⁴ on CO₂, we report on the vibrational excitation processes in N₂O via the ${}^{2}\Sigma^{+}$ resonance. We present energy-loss spectra and energy dependences of vibrational cross sections between 1 and 4 eV. Whereas the results in CO₂ could be interpreted in terms of a "two-dimensional boomerang model," the results presented in this paper differ in major ways from the case of CO₂.

Whereas the energy dependence of the resonant vibrational cross sections in CO_2 near 3.8 eV showed pronounced structure,⁴ in the case of N_2O

this energy dependence is a smoothly varying function. In addition, the energy-loss spectrum taken at the center of the ${}^{2}\Sigma^{+}$ resonance in N₂O shows a relatively short progression of vibrational modes (up to the seventh vibrational quantum number) compared to CO₂, where vibrational modes with quantum numbers up to the 20th can be observed at the center of the resonance. Using the "impulselimit" theory,¹¹ Dubé and Herzenberg¹² can account for all the experimental observations in N₂O.

II. EXPERIMENT

The apparatus used for the present study consists of a rotatable hemispherical electrostatic monochromator and a similar fixed analyzer, with a molecular beam crossing the path of the electrons in the collision region. This system has been described in detail by Boness and Schulz.⁴ The energy resolution and the signal intensity for elastically scattered electrons have been significantly improved by Wong and Schulz.¹³

In the present experiment, the apparatus resolution (FWHM) is set to be 22 meV and the scattering angle is fixed at 40°. The energy scale was calibrated against the first peak at 1.93 eV in the excitation function of the first vibrational level in N_2 , by admixing a small amount of this gas to the N_2O molecular beam.

Absolute differential cross sections for vibrational excitation in N_2O are obtained in two steps, as previously described.¹³ First we measure the ratios of inelastic to elastic differential cross sections from the energy-loss spectrum; then the elastic differential cross section in N_2O is obtained by comparing the elastically scattered cur-

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rent in N_2O with that in He at the same pressure and by normalizing to the known differential cross section of helium as calculated by Labahn and Callaway.¹⁴

III. RESULTS

A. Energy-loss spectra

Energy-loss spectra obtained at incident energies of 0.70, 2.30, and 4.00 eV, respectively, and at a scattering angle of 40° are shown in Fig. 1. At an incident energy of 2.30 eV, the vibrational cross sections (except for the fundamental modes) are almost an order of magnitude larger than at the other two energies shown in Fig. 1; also, the energy-loss spectrum at 2.30 eV shows many more vibrational modes than the spectra at 4.0 and 0.70 eV. These observations show the contribution of the ${}^{2}\Sigma^{+}$ resonance to the vibrational excitation. It should be noted that the excitation to the *fundamental* modes show a significant nonresonant contribution, which is especially pronounced for the 001 mode.¹²

The data of Fig. 1 also suggest that at least three separate series of vibrational modes are populated via the resonance. The location of the energy-loss peaks is in good agreement with the location of the vibrational series, n00 (symmetric



FIG. 1. Energy-loss spectra obtained at an angle of observation of 40° and incident energies of 0.70, 2.30, and 4.00 eV, respectively. On the top of the figure we indicate the calculated positions for the vibrational progressions n00, n10, (n-3)02, n01. The small peaks to the left of the zero-energy peak result from the deexcitation of the N₂O molecules which are in the 010 vibrational state (superelastic collisions).

stretch mode), n10 (symmetric stretch mode plus one quantum of bending), and n01 (symmetric stretch mode plus one quantum of asymmetric stretch mode). The positions of these levels, calculated from the fundamental frequencies and the anharmonic coefficients given by Herzberg,¹⁵ are indicated at the top of Fig. 1 and listed in Table I. However, for energy losses equal to or larger than the energy of the 310 mode we have an energy coincidence with the n02 series (symmetric stretch mode plus two quanta of asymmetric stretch mode). Thus we cannot resolve experimentally energyloss peaks resulting from the excitation of the n10mode from those of the (n-3)02 mode, for n > 3. To be specific, our experiment does not have sufficient resolution to resolve the 310 mode from the 002 mode, the 410 mode from the 102 mode, etc. The first two columns of Table I show the appropriate energies.

B. Energy dependence and magnitude of cross sections

Figure 2 shows the energy dependence of the differential vibrational cross sections at 40° for the excitation of the 110 and 200 modes of N₂O. These curves, with a peak near 2.3 eV, exhibit no fine structure.

The absolute value of the differential *elastic* cross section in N₂O, at 2.3 eV and 40° , has been measured as described above, and found to be $(6.4 \pm 1.9) \times 10^{-17} \text{ cm}^2/\text{sr}$, and the values of the differential vibrational cross sections for the 200 and 110 modes indicated in Fig. 2 are deduced from this value of the elastic cross section and from the energy-loss spectrum at 2.30 eV. Table II lists the absolute values of the differential cross sections, obtained in the same manner. The accuracy of the elastic cross section is $\pm 30\%$ and that of the inelastic cross sections is $\pm 35\%$. If the total cross section is desired to an accuracy of about $\pm 50\%$, multiply the differential cross sections of Table II by 4π . To the accuracy quoted above, this factor is good for either isotropic, $p\sigma$, or $d\sigma$ scattering.¹² As in the case⁴ of CO₂, we expect the excitation of different final vibrational modes to exhibit different angular distributions of electrons, because the symmetries of the final states are different.

C. Ratios of vibrational cross sections

Another prominent feature of the vibrational excitation processes in N_2O is the attenuation in amplitude of peaks which are members of the same series. Figure 3 shows the magnitude of the vibrational cross sections at 2.3 eV plotted against the quantum number *n* for the three series, n00, n10,

	Calc	culated energy le	vels (eV)		Experimental position of energy-loss peak (eV):	
n	<i>n</i> 10	(n-3)02	<i>n</i> 00	<i>n</i> 01	$error \pm 0.010 eV$	
0	0.073				0.073	
				0.275	0.276	
			0.159		0.158	
1	0.232				0.232	
				0.431	0.430	
			0.317		0.317	
2	0.391				0.390	
				0.586	0.585	
			0.475		0.473	
3	0.549	0.548			0.547	
				0.741	0.737	
4			0.632		0.630	
	0.707	0.701			0.700	
				0.894	0.890	
			0.788		0.780	
5	0.863	0.853			0.853	
				1.047	1.04	
			0.943		0.938	
6	1.019	1.004			0.995	
				1.199		
7	1		1.097		1.09	
	1.174	1.154		1.351		

TABLE I. Vibrational energy levels in N₂O. In order to compare the energies of the n10 mode with the n02 mode and to show that these modes are nearly coincident in energy, we "shifted" the energies n02 series by three quanta of the symmetric stretch mode. Hence the notation (n-3)02, whose lowest value for n=3 corresponds to the 002 mode at 0.548 eV.

and n01. For the n00 and n01 series, the vibrational cross sections decrease exponentially with the quantum number n. This is not the case, however, for the n10 series. We have already pointed out that the n10 series may have an admixture of the (n-3)02 series, since the two series are energetically indistinguishable for $n \ge 3$. We shall discuss this point in Sec. IV.



FIG. 2. Energy dependence of the differential cross sections for the 200 and 110 modes. The absence of any structure in these curves points to the possibility that a shortlived resonance is involved in populating the vibrational states in this energy range. The estimated error for the cross section scale is about 35%.

Inc	Incident electron energy (eV)			
0.70	1.00	2.30	4.00	
60	240	640	310	
.5	8.5	45	11	
.5	2.5	12	1.3	
ת	0.8	5.0	1.0	
×	×	3.1	×	
×	×	2.7	×	
×	×	2.2	×	
×	×	1.6	×	
21	26	96	10	
2.4	4.2	42	1.7	
×	1.2	18	0.8	
×	×	8.7	×	
×	×	5.4	×	
×	×	3.0	×	
×	×	1.3	×	
20	18	28	2.4	
).6	1.0	15	1.1	
×	×	12	0.7	
×	×	7.9	×	
×	×	5.6	×	
×	×	3.3	×	
	Inc 0.70 1.5 1.5 × a × × × × × × × × × × 21 2.4 × × × × × × 20 0.6 × ×	Incident elect: 0.70 1.00 260 240 1.5 8.5 2.5 2.5 \times 0.8 \times \times \times \times \times \times 21 26 2.4 4.2 \times \times \times \times 20 18 0.6 1.0 \times	Incident electron energy (eV) 0.70 1.00 2.30 2.60 240 640 4.5 8.5 45 5 2.5 12 \times 0.8 5.0 \times \times 3.1 \times \times 2.7 \times \times 2.2 \times \times 1.6 21 26 96 2.4 4.2 42 \times 1.2 18 \times \times 3.0 \times \times 1.3 20 18 28 0.6 1.0 15 \times \times 12 \times \times 7.9 \times \times 5.6 \times \times 3.3	

TABLE II. Absolute magnitude of differential cross sections at 40° in N_2O , in units of 10^{-19} cm²/sr.

^a× indicates a cross section smaller than 0.6×10^{-19} cm²/sr, i.e., below our present detection sensitivity.



FIG. 3. Magnitude of vibrational cross sections for the series, n00, n01, and [n10+(n-3)02] vs the quantum number n. The two latter series, n10 and (n-3)02, are not distinguishable for n > 3. The theory of Dubé and Herzenberg shows that both these modes contribute to vibrational excitation.

IV. DISCUSSION

The energy dependence of the vibrational cross sections shown in Fig. 2 does not exhibit structure. In a *diatomic system*, the absence of structure can be interpreted in one of two ways: (i) the potential-energy curve which is responsible for the vibrational cross section is attractive but the lifetime is short compared to the vibration time, or (ii) the potential-energy curve is repulsive, in which case the lifetime can be long or short.

The ${}^{2}\Sigma^{+}$ state of N₂O⁻ which is responsible for the vibrational excitation around an electron energy of 2.3 eV also leads to the formation of O⁻ by dissociative attachment.¹⁰ The potential-energy curve for this state must therefore be of a repulsive nature in some cut through the three-dimensional potential-energy surface. However, in a triatomic system (XYZ) the consequences of a repulsive-type surface are more complex than is the case for diatomic molecules: The wave packet associated with the resonance in a triatomic system can, under certain circumstances, perform vibrations (or a "boomerang motion") in a direction other than that leading to dissociation. This type of motion can cause structure in the vibrational cross section even above the dissociation limit for the negative ion, e.g., $X^- + YZ$. An example of such a phenomenon is the structure which is observed for the elastic and the vibrational cross sections in CO_2 above an energy of 4.1 eV, i.e., above the onset for dissociative attachment.^{16,4} Thus the absence of structure in a triatomic system even with a repulsive surface for the resonance suggests that the lifetime of the resonance is relatively short.

Figure 3 shows that for the experimentally resolved vibrational series n00 and n01, the magnitude of the vibrational cross section decreases exponentially with the vibrational quantum number n. The trend of the branching ratio^{1,11} is reminiscent of that observed in the vibrational and rotational excitation of the diatomic molecule H_2 via the short-lived ${}^{2}\Sigma_{u}^{+}$ shape resonance near 4 eV. This similarity suggests that the ${}^{2}\Sigma^{+}$ shape resonance in N₂O is short lived. Calculations have been performed by Dubé and Herzenberg,¹² within the framework of the "impulse approximation." By obtaining a good fit to the energy dependence for the vibrational modes 200 and 110 of Fig. 1, they establish that the lifetime of the $N_2O^{-}(^{2}\Sigma^{+})$ resonance is indeed short. Their value for the width, Γ , is about 0.7 eV in the center of the Franck-Condon region and it decreases for larger internuclear separations.^{17,18} When the width is used to obtain the branching ratios of the vibrational series of Fig. 3, very good agreement results for the experimentally resolved series n00 and n01.

The theoretical fit to the remaining curve of Fig. 3 is also good, but the theory of Dubé and Herzenberg shows that this curve is composed of two parts, namely, the *n*10 mode and (n-3)02 mode. Experimentally, these two series are indistinguishable in the present experiment and it is only through reliance on theory that we can arrive at this interpretation.

The good agreement between the present experiment and the impulse-limit theory shows that the approximations developed for the case of diatomic molecules are applicable to triatomic molecules as well. Thus the N₂O⁻($^{2}\Sigma^{+}$) resonance is analogous to the H₂⁻($^{2}\Sigma^{+}$) resonance and we have previously shown⁴ that the CO₂⁻($^{2}\Pi_{u}$) resonance can be understood in terms of the "boomerang" intermediate-lifetime model which was originally developed for the N₂⁻($^{2}\Pi_{g}$) resonance. Hopefully, these relatively simple theories will be applicable to more complex molecules as well.

We conclude that the ${}^{2}\Sigma^{+}$ shape resonance in N₂O is short lived and that the impulse approximation must be invoked to interpret the vibrational excitation. Four series of vibrational modes are populated via the ${}^{2}\Sigma^{+}$ resonance, namely, n00, n01, n10, and n02. The last two are coincident in en-

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ergy above the 002 mode.

Below the energy range of the ${}^{2}\Sigma^{+}$ resonance (i.e., near 1 eV, see Table II), only the fundamental modes have an appreciable cross section (probably resulting from a direct process), and of those the 001 mode stands out. This effect is reminiscent of the behavior of the 001 excitation in CO_2 . In the latter case, a peak is observed¹⁹ in the excitation of the 001 mode at an electron energy of 0.9 eV. This peak can be attributed to the transition-dipole moment^{20,21} associated with the 001 mode, rather than to a resonance. In this respect, the case of CO_2 is more clear-cut because the ${}^2\Pi_u$ resonance at 3.8 eV is the lowest-lying shape resonance and thus a process around 1 eV must have its origin in direct excitation. The ${}^{2}\Sigma^{+}$ resonance in N₂O at 2.3 eV, which is the subject of this paper, is the second shape resonance of N₂O, the first being the ²Π resonance near zero energy.¹⁰

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