Electron scattering from NO and N_2O below 10 eV

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Total electron scattering cross sections for NO and N_2O in the energy range 0–10 eV were obtained from exponential attenuation in a straight-line collision chamber without a confining magnetic field. Good agreement is obtained with previous measurements where available. For NO, cross sections have been obtained for the first time for resonance structure in the energy range 0–2.5 eV. There appear to be small, sharp resonances between the large resonances. For both NO and N_2O the cross section is observed to increase rapidly at very low energies. Structure in the cross sections is interpreted in terms of electronic states of NO^- and N_2O^-.

INTRODUCTION

Total cross sections for electron scattering from NO and N_2O were measured many years ago by Brüche[1] and by Ramsauer and Kollath.[2] Since the advent of high energy resolution electron spectrometers, no comparable measurements have been made. Relative transmission measurements have been made for NO in the range 0–2.5 eV[3-5] and for N_2O in the range 0–6 eV,[3,6] but it is not possible to obtain cross sections from these results. Sharp resonances in NO were observed by Sanche and Schulz[7] by measuring the derivative of the transmitted electron current. The derivative method is relatively insensitive to broad resonances. Therefore we decided to measure relative total scattering cross sections for N_2O and NO in the energy range 0–10 eV in an attempt to locate broad resonances and to determine the absolute size of the sharp resonances observed by Sanche and Schulz.[6,7] The absolute cross-section measurements were also carried out to an energy below 0.1 eV. For both NO and N_2O, a rapidly rising cross section is observed and tentatively ascribed to the electron–multipole interaction.

PROCEDURE

The apparatus used in these measurements has been previously described,[8] and a detailed description will be given of the procedures used to obtain total electron scattering cross sections.[9] Briefly, a high resolution retarding potential difference electron monochromator is used, and cross sections are obtained from exponential attenuation in a straight-line collision chamber without a confining magnetic field. Relative pressures in the scattering chamber were measured with an ionization gauge in the vacuum chamber surrounding the electron spectrometer. The temperature of the scattering chamber is approximately 430 °K, caused by heat flow from the electron gun. Relative cross sections for NO were normalized to 9.0×10^{-16} cm^2 at 5 eV[1] and for N_2O to 9.5×10^{-16} cm^2 at 4 eV.[1,2]

The energy scale was calibrated by mixing helium with the gas being measured and observing the helium resonance near 19.3 eV. Weighting the results of Kuyatt *et al.*[10] (19.31 ± 0.03 eV), Sanche and Schulz[11] (19.34 ± 0.02 eV), Cvejanovich, Comer, and Read[12] (19.355 ± 0.008 eV), and Read[13] (19.367 ± 0.009 eV), according to their stated errors we adopt the value 19.35 eV. The estimated uncertainty of the energy scale is ±30 meV.

At a given pressure, many sweeps over the energy range of interest were accumulated and averaged by an on-line computer. A typical run for N_2O consisted of 20 sweeps at each of three pressures with an attenuation range of about three to one. For NO, 10 sweeps were made at each pressure. Relative cross sections were calculated from the two pairs of successive pressures and averaged. Typically the two cross sections differed from their average by less than 5% for N_2O and about 10%–20% for NO. Cross sections from several runs were then averaged to give the final results. In the case of NO, small differences in the energy scale for different runs caused the averaging to degrade the resolution of the structure between 0 and 2 eV. Therefore this region has been taken from a high resolution run and normalized to the higher energy portion of the cross section.

A test of exponential attenuation for NO at several electron energies is shown in Fig. 1.

RESULTS

NO

The total scattering cross section for NO is shown in Figs. 2(a) and 2(b). Agreement with the previous measurements of Brüche[1] is good. The large increase in cross section near zero energy is real and not an instrumental effect. Measurements in the same energy range for helium[9] show a decrease in cross section.

Structure in the energy range 0–2.5 eV is in qualitative agreement with previous relative transmission measurements.[3-5] There are a series of sharp peaks in the total scattering cross sections with a vibrational spacing of about 165 meV which have been interpreted[14,15] as vibrationally excited states of a bound $^3\Sigma^-$ NO^- state with a binding energy of 54 meV.[16] The structure between 0 and 2 eV is shown at higher resolution in transmission in Figs. 3(a)–3(c). Here the sharp dips correspond to the peaks in the total cross section. Note

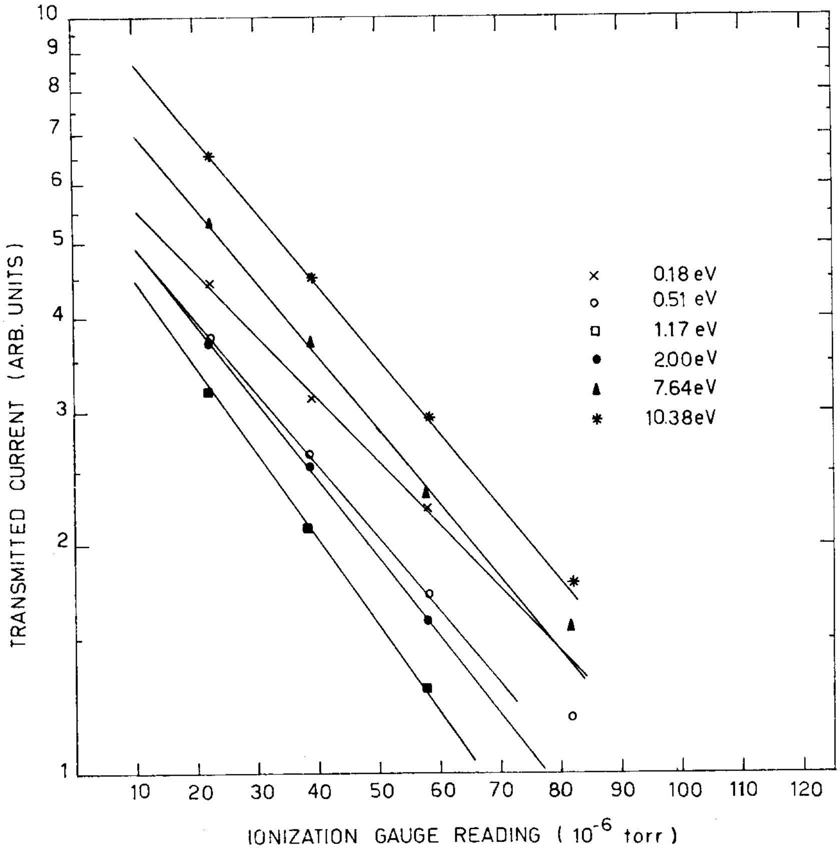

FIG. 1. Electron beam attenuation as a function of NO pressure, demonstrating conformance to exponential attenuation.

that there appear to be small sharp resonances between the large resonances.

Table I gives the measured positions of the NO resonances together with some previous measurements. Our measured spacings decrease then increase with increasing vibrational quantum number, while previous measurements[3–5,15,16] appeared to give constant spacing. Note that there is also a variation in peak height which correlates with the variation in spacing and gives the appearance of "beating" between two series of resonances. The average spacing is ≈160 meV, in agreement with previous measurements.

Transmission measurements with very high sensitivity were made in the energy range 5–8 eV by averaging in the on-line computer for about 10 h. By subtracting a linear background from the data, sharp structures were observed which roughly correlate with resonances observed by Sanche and Schulz using derivative spectroscopy. However, the signal-to-noise ratio of these very small structures must be improved before data can be presented.

N_2O

The total scattering cross section for N_2O is shown in Fig. 4. Agreement with the previous measurements of Ramsauer and Kollath[2] is good. However, Brüche[1] found the broad peak near 2.2 eV to be bigger than our measurement. This peak is in qualitative agreement with a previous relative transmission measurement.[3–5,7] No sharp structure has been found. A large increase in cross section is observed near zero energy.

ANALYSIS OF NO AND N_2O RESONANCES

The theory of electron resonance scattering with molecules has been presented many times.[18,19] For an isolated resonance the resonant scattering cross section is given by the Breit–Wigner formula and exhibits resonant behavior near the vibronic energy levels. Analysis of resonant scattering then requires a knowledge of the lowest energy electronic states of NO^- and N_2O^-. A qualitative review of these electronic states will be given first then a brief application of these states to analyze the scattering.

ELECTRONIC STATES

NO^-

Four electronic states correlate with the ground state asymptote, $N(^4S)+O^-(^2P)$, the $^3\Sigma^-$, $^5\Pi$, $^3\Pi$, and $^5\Sigma^-$. Of these the $^3\Sigma^-$ is the ground state for which the dominant electronic configuration in the neighborhood of the equilibrium separation is $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4 \times 2\pi^2$. This configuration can also be coupled $^1\Delta$ and $^1\Sigma^+$. From the isoelectronic O_2 molecule we know that the $^3\Sigma^-$, $^1\Delta$, and $^1\Sigma^+$ states lie close in energy. In the case of O_2 all three states correlate with the asymptotic ground state, $O(^3P)+O(^3P)$, but only the $^3\Sigma^-$ state correlates with $N(^4S)+O^-(^2P)$ for NO^-. Both the $^1\Delta$ and $^1\Sigma^+$ curves correlate adiabatically to the $N^-(^3P)+O(^3P)$ asymptote. Since the nitrogen atom does not have a positive electron affinity, this asymptote can be taken equal to the neutral ground state asymptote, $N(^4S)+O(^3P)$. A self-consistent-field calculation of the energies of the $^3\Sigma^-$ and $^1\Delta$ states at $R=2.1747$ a.u. yielded an excitation energy of 2.2 eV. A comparable calcula-

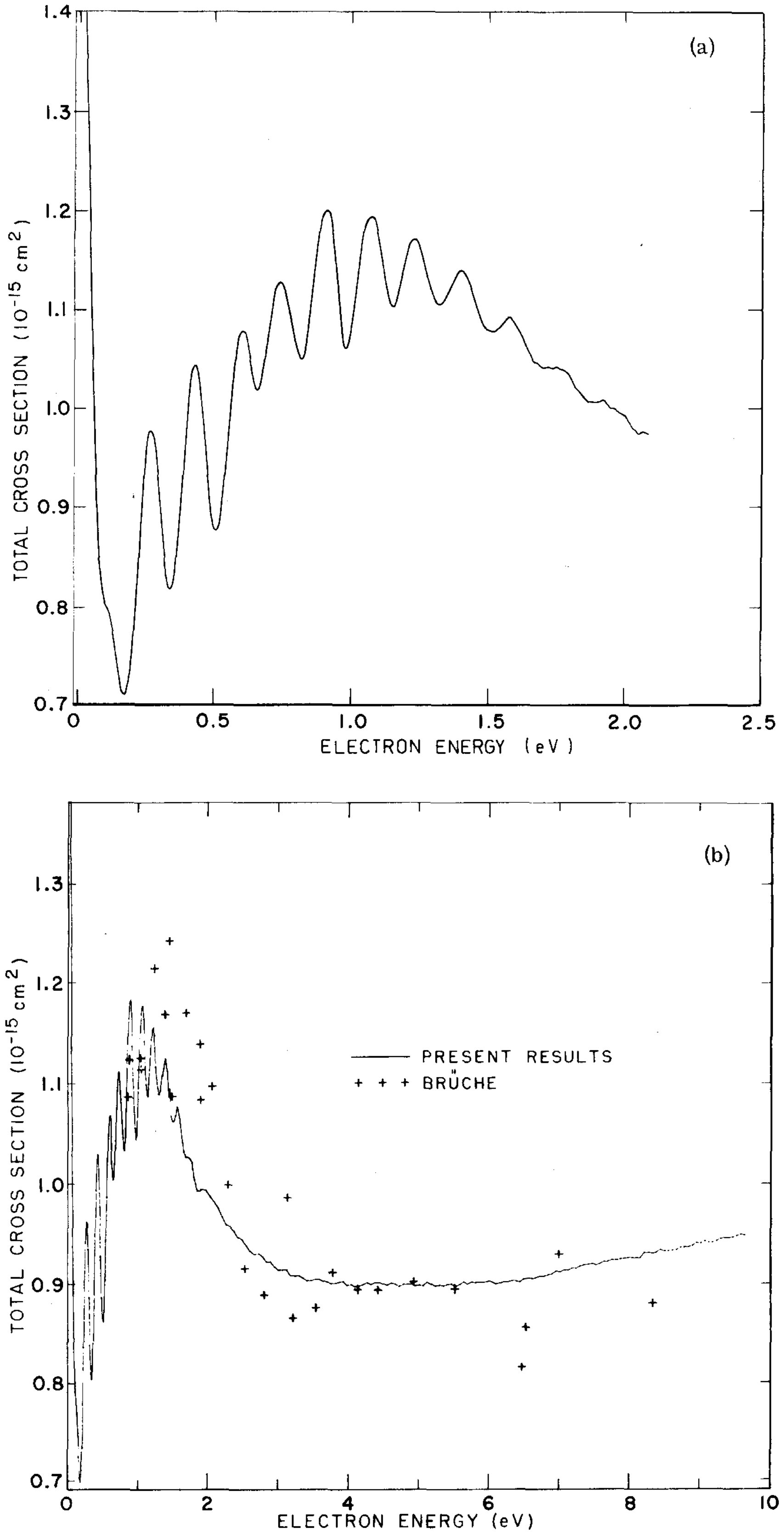

FIG. 2. Total scattering cross section for NO. Normalized to 9.0×10^{-16} cm^2 at 5 eV. (a) 0–1.5 eV, (b) 0–9.5 eV. Data of Ref. 1 obtained from L. J. Kieffer, At. Data 2, 293, 312 (1971).

tion of the analogous states in O_2 yielded an excitation energy of 1.29 eV which is to be compared with an experimental excitation energy of 0.98 eV. As in the case of O_2 the spectroscopic constants for all three NO^- states are expected to be similar. The electron affinity and spectroscopic constants of the $^3\Sigma^-$ NO^- state have been reported.[17] Using this information it is possible to draw a very approximate potential energy diagram of the lowest three states of NO^- relative to the ground state of NO, the $X\,^2\Pi$ as shown in Fig. 5.

N_2O^-

A brief sketch of the low-lying negative-ion states of N_2O^- has been given by Bardsley.[20] The ground state of N_2O is linear and the only excited valence-type orbital at the equilibrium internuclear geometry calculated by molecular orbital theory[21] is the 3π. This orbital is similar to the $2\pi_u$ orbital of CO_2, and the isoelectronic systems can be compared. From both theory[22] and experiment[23] it is known that the CO_2^- ground state is bent and the CO internuclear distance is greater than that in the neutral molecule. A similar situation, of course, is predicted for N_2O.[24] The excited states of N_2O are somewhat lower than those of CO_2, and a comparison of CO_2^- calculated energy curves would permit an inference with regard to the N_2O^- curves.

Attachment of a $2\pi_u$ electron to CO_2 yields a $^2\Pi_u$ configuration which yields two states when the molecule is bent symmetrically, a lower energy $^2A_1$ and a $^2B_1$. An SCF calculation of the $^2A_1$ state shows it to be bound relative to the neutral $^1A_1$ curve at the ion equilibrium angle. From this calculation it is possible to deduce that the CO_2^- in the gas phase would be metastable. Recent experimental work has reached the same conclusion.[25]

The $^2A'$ ground state of N_2O^- would then be expected to be bound relative to the neutral curve much as depicted by Bardsley. The excited $^2A''$ state which correlates with the $^2\Pi$ state at 180° would be entirely above the neutral curve, and the probability of autodetachment would be very high.

An important feature of the CO_2^- calculation shows that the CO internuclear distance is about 10% greater than the neutral value. This would be expected for N_2O^- as well in the $^2A'$ state.

TABLE I. Resonances in NO.

Resonance (see Fig. 3)	Spence and Schulz[a] (Ref. 11)	Energy[b] (meV) Present	Spacings Present
1	114	100	165 ± 5
2	280	265	165 ± 5
3	444	430	165 ± 5
4	606	595	140 ± 5
5	766	735	165 ± 5
6	924	900	175 ± 5
7	1080	1075	165 ± 10
8		1245	165 ± 10
9		1410	175 ± 10
10		1585	175 ± 10
11		1760	175 ± 10
12		1935	
1′		160	175 ± 20
2′		335	165 ± 20
3′		500	160 ± 40
4′		660	

[a] Calculated from $\omega_e = 170$ meV, $\omega_e x_e = 1$ meV.
[b] Absolute values are believed accurate within ~ 30 meV.

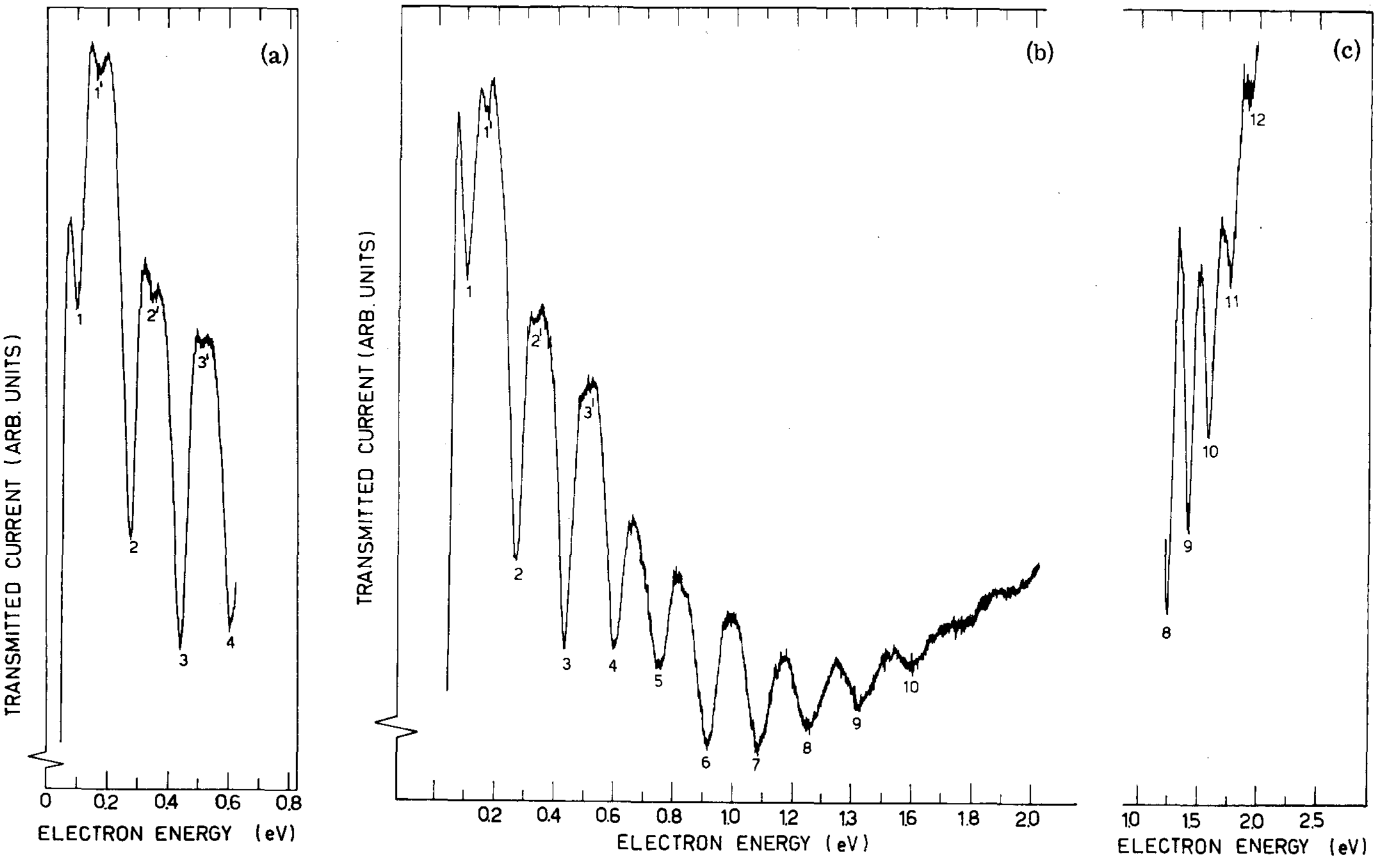

FIG. 3. Transmission resonances in NO. (a) 0–0.6 eV, (b) 0–2 eV, (c) 1.2–2 eV expanded scale.

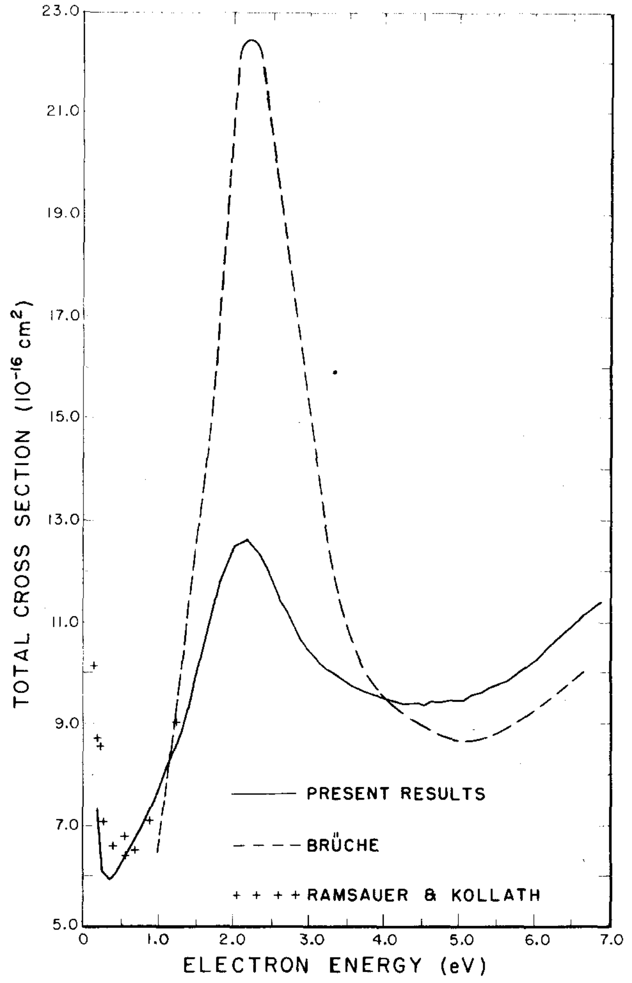

FIG. 4. Total scattering cross section for N_2O. Normalized to 9.5×10^{-16} cm^2 at 4 eV. Data of Refs. 1 and 2 obtained from J. Kieffer, At. Data 2, 293, 315 (1971).

Bardsley[20] and Chantry[26] have considered other excited N_2O^- states which arise by adding an electron to the 8σ orbital. As shown explicitly by Chantry this state is expected to have a very extended N–O equilibrium distance. Such a bound negative ion state with a very extended equilibrium internuclear distance is exemplified by the ${}^4\Sigma_u^-$ state in O_2^- which has an $r_e = 3.2$ a.u. compared to the ground neutral state $X\,{}^3\Sigma_g^-$, $r_e = 2.1$ a.u. The r_e (N–O) for this state is very much larger than for the ${}^2\Pi$ ground state. The energy increases with bending angle; the state is linear. Both the ${}^2\Sigma^+$ and ${}^2\Pi$ states correlate with ground state $N_2 + O^-$. The adiabatic correlation diagram of Fig. 6 schematically describes the electronic state situation. The asymptotic adiabatic correlations are given in Table II.

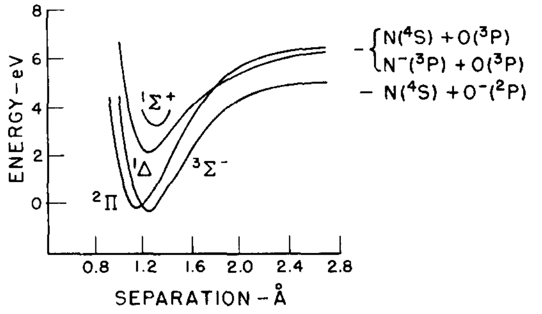

FIG. 5. Approximate potential energy diagram for NO^- and NO.

ANALYSIS OF RESONANCE SCATTERING

e+NO

The resonances observed between 0 and 2 eV incident kinetic energy can arise from only one electronic state, the ${}^3\Sigma^-$ state of NO^-. The spin–spin splitting of a ${}^3\Sigma_u^-$ state is quite small and can be neglected. The ${}^1\Delta$ state is too high in energy to affect the resonant behavior although the presence of such a state with a large detachment width could contribute to the background.

The small structures in Fig. 3 designated by the primed numbers cannot be related to any degeneracy in the resonance state. The spin-orbit splitting of 121 cm^{-1} is not resolvable in this experiment. Because the NO is considerably above room temperature an appreciable number of rotational levels can be populated and the scattering is the sum over all such states. It is difficult to see how the excited rotational levels could yield the sharp structure of Fig. 3. Another possibility arises from the fact that at the temperature of the scattering chamber the first vibrationally excited state of NO has a population of about 0.2%. Assuming some enhancement from the high pressures used to accentuate the resonance structure, one might expect additional resonances shifted downward by 233 meV. On this basis the primed resonances would be expected at 197, 362, 502, and 667 meV. The agreement with the measured energies is close enough that this possibility cannot be ruled out. Finally, there remains the possibility that the primed resonances are ghosts caused by structure in the energy distribution of the electron beam. We belive this is unlikely because such ghosts should accompany all of the resonances and because the helium 19.3 eV resonance, when observed to set the energy scale, did not show ghosts of comparable size to the primed resonances.

Electron impact cross sections for both elastic and rotational excitation collisions are known to be large for molecules with permanent dipole and quadrupole mo-

TABLE II. Asymptotic adiabatic correlations for N_2O^-.

		Energy relative to $\vert {}^2A'$	$C_{\infty v}$	C_s
O	N_2			
${}^2P$	${}^1\Sigma_g^+$	0.4	${}^2\Sigma^+$, Π	${}^2A'(2), A''$
${}^2P$	${}^3\Sigma_u^+$	6.57	${}^{2,4}\Sigma^+$, Π	${}^{2,4}A'(2), A''$
N	NO			
${}^4S$	${}^3\Sigma^-$	5.11	${}^{2,4,6}\Sigma^+$	${}^{2,4,6}A'$
${}^4S$	${}^1\Delta$	~7.1	${}^4\Delta$	${}^4A', A''$
${}^2D$	${}^3\Sigma^-$	7.49	${}^{2,4}\Sigma^+$, Π, Δ	${}^{2,4}A'(3), A''(2)$

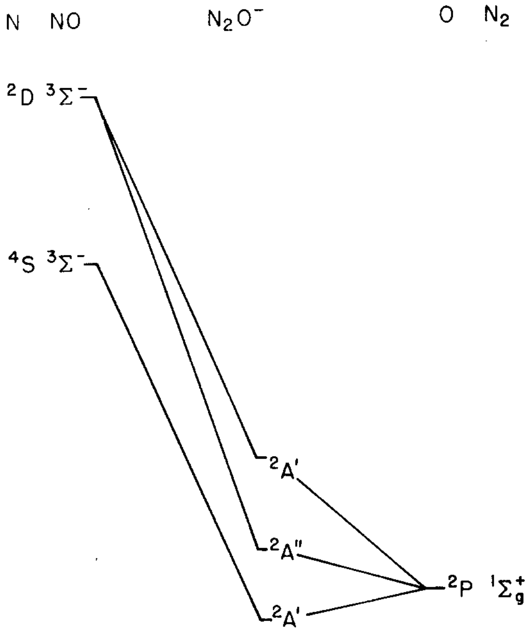

FIG. 6. Adiabatic correlation diagram for N_2O^-.

ments.[27] The maximum for the cross section for the rotational excitation is very close to the threshold and would not be observed in this study. The cross section for NO is still increasing when it has reached a value of 1.2×10^{-15} cm^2. This is still smaller than maximum cross sections predicted for a molecule such as CO by either the Born[28] or close-coupling methods.[29] Since the dipole moments of CO and NO are similar in magnitude it is plausible to ascribe this large cross section to the electron-multipole interactions.

$e+N_2O$

The analysis applied by Bardsley and Chantry to dissociative attachment is equally applicable to the vibrational excitation or total scattering. The lowest $^2A'$ resonance state in its bent state has an energy almost equal to that of the neutral N_2O. Franck–Condon factors to the low-lying vibrational levels of $^2A'$ are small but the cross section rises rapidly with decreasing energy. Nonetheless the Franck–Condon factors for the bending transition would be expected about 0.75–1 eV above zero, and the energy spacings would be expected to be appreciably smaller than for the neutral bending levels. The levels of the $^2A''$ state would be expected to have large widths. Since the energy levels of the real system are determined by mixing the $^2A'$ and $^2A''$ levels through the Renner coupling, it is not readily apparent what the vibrational level structure would be above about 1 eV. The larger widths that probably occur in this region would make observation of resonances difficult.

Stretching modes of the N_2O^- resonance state would be observable at lower energies. The Franck–Condon factors to low-lying stretching modes should be large since the equilibrium separations change by only 10%. But the stretching frequencies in the negative-ion state will be considerably less than those of the neutral N_2O since the negative ion states can correlate with ground state asymptotes while the neutral could not. The dissociation energy of the $^2A'$ state is certainly less than 1 eV. Calculations will be needed to confirm these speculations, but structure in N_2O transmission curves at low energy would be assigned to low energy stretching vibrations and bending modes and/or combination modes would be excited at energies of about 1 eV.

The major structure with a peak at about 2.3 eV has been interpreted as due to the excited $^2A'$ or $^2\Sigma^+$ state of N_2O^-.[20,30,31] The dissociative attachment production of O^- at 2.3 eV is probably due to this resonance. But the entire resonant structure to below 1 eV may be due, as suggested previously, to the overlap of structure from the $^2\Pi$ and $^2\Sigma^+$ N_2O^- states. There is no way of deciding between these states from the present data.

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