

Dissociative-electron-attachment cross sections: A comparative study of NO₂ and O₃S. A. Rangwala,^{*} E. Krishnakumar,[†] and S. V. K. Kumar[‡]*Tata Institute of Fundamental Research, Homi Bhabha Road, Mumbai 400 005, India*

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Absolute cross sections for dissociative electron attachment (DEA) to NO₂ have been measured and compared with that of O₃. A striking similarity is observed in the dissociation channels and the relative cross sections between the two molecules. This similarity is interpreted in terms of a common mechanism for electron capture to the two molecules and is exploited to characterize the nature of the NO₂ resonances in analogy with O₃, using specific quantum chemical calculations as well as experimental data. This experimental observation and its interpretation seeks to direct attention to a previously unmentioned aspect of the DEA phenomenon in relation to molecules that are isoelectronically unrelated. The observation also tends to highlight the dominance of electronic polarizability in the electron-molecule scattering potential leading to capture.

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I. INTRODUCTION

The construction of models that group atoms and molecules by their properties has been a common feature in the effort to understand them. The most successful of these has been based on the number of active electrons, starting from the construction of the Periodic Table of elements. The similarity in the spectral features of atoms and ions with the same number of electrons, properties of molecules in an isoelectronic sequence, and molecules with similar orbital configurations are other examples. Total electron scattering data on isoelectronically related N₂O and CO₂ as well as N₂ and CO show almost identical behavior, as does the total positron scattering data [1]. Similarities in the resonant low-energy electron scattering from N₂ and CO have also been discussed [2]. Even in the specific case of electron attachment, a similarity in behavior related to electron affinity and near-zero energy resonances have been seen for several halogen-containing molecules. Another aspect that has been discussed in some detail is the possibility of sustaining bound negative ion states as a function of the permanent dipole moment of the molecules [3]. However, to our knowledge there exists no other attempt to look for common behavior in molecules, as far as the electron attachment properties are concerned. We present the possibility of one such situation, where a common behavior is in evidence in two isoelectronically unrelated molecules.

The phenomenon of dissociative electron attachment (DEA) to molecules has generated considerable interest as it occurs in competition with electronic processes (i.e., the autodetachment of an electron). It is also a resonant process, a fact that is evident from its spectral discreteness. Briefly, DEA can be described as a two-step process. Step one entails the resonant capture of a free electron by the molecule lead-

ing to the formation of a complex negative ion. Step two concerns the decay of this negative ion via either electron ejection or dissociation into neutral and negative ion fragments. The latter channel is termed DEA.

However, the complexity of DEA has made its theoretical description very challenging. Theoretical work is computationally intensive and has not been able to reproduce adequately the experimental results, except in the simplest cases. Hence the full-scale treatment of polyatomic molecules is unlikely in the near future [4]. Thus the situation underlines the need to experimentally identify similarities and draw phenomenological conclusions wherever possible.

This approach too has its difficulties as, in order to see obvious connections between the DEA spectrum of two different molecules, one must have a similarity between the capture mechanisms that is not destroyed by the nature of the potential-energy surfaces along which the ion complex dissociates. The fact that most molecular negative ions so formed have more than one dissociation channel available could also serve to disguise the common processes if they exist. Despite this limitation, we appear to have come across two triatomic systems in which DEA spectra are too strikingly similar to ignore a possible connection in the capture channel.

Though relative cross sections for the DEA process have been obtained for NO₂ [5,6], there exist no data on absolute cross sections. Considering the importance of these data for applications such as control of atmospheric pollution, since NO₂ is a major pollutant, we have measured the absolute cross sections for dissociative electron attachment to NO₂. The data show remarkable similarities to the cross sections obtained for the same process in O₃ [7].

II. EXPERIMENT

The experimental technique used for these measurements has been discussed in detail elsewhere [7,8]. A magnetically collimated and pulsed electron beam of variable energy is crossed with an effusive molecular beam producing negative ions. The ions are extracted into a segmented time-of-flight (TOF) mass spectrometer using a pulsed electric field applied to the interaction region a few tens of nanosecond after the

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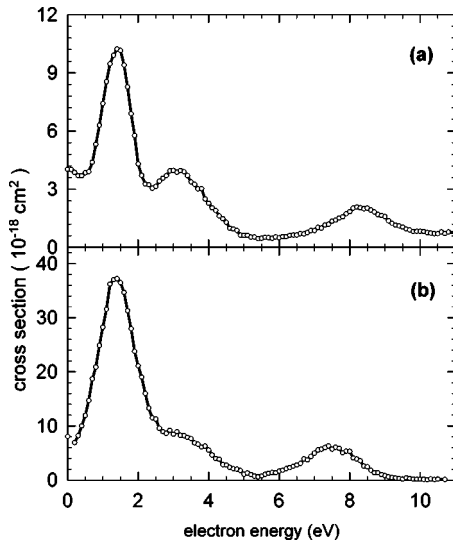


FIG. 1. O^- cross section as a function of incident electron energy from (a) NO_2 and (b) O_3 .

electron pulse. The pulsed nature of the ion extraction field makes it possible to apply a very large electric field to the interaction region without affecting the electron beam as it does not overlap with the electron pulse. The ions entering the TOF mass spectrometer are transmitted and focused onto a detector without loss using the multielement flight tube, which acts as an electrostatic lens assembly. The detector is a channel electron multiplier operated in the pulse-counting mode. The TOF mass spectra of the anions were obtained using a time-to-amplitude converter (TAC) followed by a pulse height analyzer.

To begin with, the ion yield curves were measured by selecting appropriate time windows in the TAC and storing the signals as a function of electron energy using a general purpose interface bus (GPIB)-based data-acquisition system. The cross sections were put on an absolute scale by using the relative flow technique [9] and O^- from O_2 as the standard [10].

The mass spectrum of the DEA fragment ions observed in our experiment has two distinct ion peaks. The dominant ion peak is O^- and the other peak is a combination of NO^- and O_2^- ions. These ions have been seen in an earlier, qualitative measurement of DEA from NO_2 [6]. In our experiment, the complete collection of the ions formed in the interaction region comes at the price of good mass resolution, hence the difficulty in separating the NO^- and the O_2^- ions. Our measurements show that O^- cross sections are approximately two orders of magnitude larger than the combined NO^- and O_2^- cross sections.

III. RESULTS AND DISCUSSION

Figure 1(a) illustrates the variation of the O^- DEA cross section from NO_2 as a function of incident electron energy. The measured absolute cross sections in the range 0 – 11.0 eV are given in Table I. The details of the method of error estimation for similar measurements have been discussed in an earlier publication [8]. The cross section at the

TABLE I. Table of absolute cross section for the formation of O^- from NO_2 by dissociative electron attachment as a function of incident electron energy.

Electron energy (eV)	$\sigma 10^{-18} \text{ (cm}^2\text{)}$	Electron energy (eV)	$\sigma 10^{-16} \text{ (cm}^2\text{)}$
0.0	4.02	5.5	0.47
0.1	4.01	5.6	0.51
0.2	3.86	5.7	0.50
0.3	3.69	5.8	0.46
0.4	3.69	5.9	0.54
0.5	3.85	6.0	0.49
0.6	3.90	6.1	0.55
0.7	4.39	6.2	0.55
0.8	5.32	6.3	0.62
0.9	6.29	6.4	0.63
1.0	7.42	6.5	0.63
1.1	8.55	6.6	0.71
1.2	9.47	6.7	0.69
1.3	9.90	6.8	0.76
1.4	10.23	6.9	0.87
1.5	10.15	7.0	0.87
1.6	9.40	7.1	1.03
1.7	8.27	7.2	0.99
1.8	6.89	7.3	1.16
1.9	5.76	7.4	1.19
2.0	4.30	7.5	1.35
2.1	3.71	7.6	1.41
2.2	3.27	7.7	1.51
2.3	3.23	7.8	1.57
2.4	3.04	7.9	1.73
2.5	3.14	8.0	1.84
2.6	3.41	8.1	2.03
2.7	3.56	8.2	2.08
2.8	3.70	8.3	2.04
2.9	3.94	8.4	1.99
3.0	3.96	8.5	2.03
3.1	3.87	8.6	1.92
3.2	3.96	8.7	1.82
3.3	3.90	8.8	1.69
3.4	3.70	8.9	1.64
3.5	3.37	9.0	1.58
3.6	3.25	9.1	1.37
3.7	3.01	9.2	1.24
3.8	3.03	9.3	1.14
3.9	2.50	9.4	1.11
4.0	2.27	9.5	1.05
4.1	2.04	9.6	0.95
4.2	1.90	9.7	0.89
4.3	1.62	9.8	0.82
4.4	1.48	9.9	0.83
4.5	1.29	10.0	0.83
4.6	0.99	10.1	0.82
4.7	0.95	10.2	0.76
4.8	0.87	10.3	0.74
4.9	0.62	10.4	0.71
5.0	0.62	10.5	0.70
5.1	0.62	10.6	0.79
5.2	0.52	10.7	0.71
5.3	0.53	10.8	0.79
5.4	0.45	11.0	0.76

TABLE II. Positions of the resonance peaks observed in the O⁻ DEA channel for NO₂ and O₃.

NO ₂	O ₃
1.4 eV	1.2 eV
3.1 eV	3.0 eV
8.3 eV	7.5 eV

1.4 eV peak is 1.02×10^{-17} cm², with the one-sigma error at the peak cross section being 13%. The uncertainty in the electron energy scale is 0.1 eV and the half-width of the electron energy distribution is about 0.5 eV. Figure 1(b) shows the variation in the cross section for the formation of O⁻ ions from O₃ [7] as a function of incident electron energy. The qualitative similarity between the two sets of data is remarkable given the fact that we are comparing the cross sections from different molecules. For instance, a look at the DEA signal in the O⁻ fragment ion channel from several triatomic molecules shows large differences in both the structure and cross sections [11]. In contrast, the DEA cross sections for the O⁻ ions from NO₂ and O₃ are similar to the order of magnitude, the difference being a factor of 3.7. The main features are the three peaks, which are listed in Table II. Thus the presence of both qualitative and quantitative agreement in the DEA cross sections for the O⁻ ion fragment from both of these molecules demands an explanation.

Since the properties of NO₂ and O₃ are substantially dissimilar, the most striking being the difference in the spin multiplicity of the ground state of the two molecules, a reasonable explanation for the observed similarities must transcend the individual peculiarities of the two molecules. The dissociation channels available to the negative ion complex formed are governed by the precise nature of the potential-energy surfaces and are therefore dependent on the molecule. If, however, as in the present case (see Fig. 1), ion signals from different molecules in the dominant DEA channel show very similar behavior, it implies that the resonant free-electron capture occurs to both these molecules at the same energies. In such a situation the electron capture process may have a common mechanism, provided the molecular properties instrumental for capture of the free electron are found to be in agreement. It can also be concluded that the observed similarity in only the O⁻ channel of the DEA phenomenon is sufficient to argue in favor of a common electron capture mechanism because similarity at the end of the second step in the dominant ion channel is a sufficient signature for similarity in the first step, i.e., that of electron capture. That the similarity in the capture channel is reflected in the DEA cross section may be a fortuitous occurrence considering that the molecules are triatomic in nature and that there exist different dissociation pathways. However, the fact that formation of O⁻ plus the corresponding neutral fragment channel is overwhelmingly dominant shows that other dissociation pathways are weak and the systems may be effectively treated as a two-center system with the O–O₂ bond (for O₃) and O–NO bond (for NO₂) being the active bonds. This simplification to a near diatomic system may have prevented the camouflaging of the similarity in the capture channel so

that it (the similarity) could appear in the DEA cross sections.

The mechanism for free electron capture can in general be either a shape resonance (single particle or core excited) or a Feshbach resonance. Shape resonances are characterized by the trapping of the incident particle (electron) in the resultant potential barrier formed due to the combination of the attractive part of the potential and the repulsive angular momentum barrier. Feshbach resonances result from the trapping of the projectile in the potential of the excited neutral state. The excitation is achieved by the interaction of the ground-state neutral with the incoming projectile.

Experimentally, most of the resonances seen in the DEA as well as the scattering channels from O₃ have been assigned as shape resonances. These assignments have been made by Allan *et al.* [12], except that some preliminary calculations predict that the 1.3 eV peak is likely to be a Feshbach resonance [13]. Two additional structures seen in the electron scattering channel at 4.2 and 6.6 eV have also been assigned as single-particle shape resonances [12]. The DEA peak seen at 7.5 eV by Allan *et al.* has been assigned as a core excited Feshbach resonance, but no motivation has been provided for this assignment. However, a recent calculation of the resonances in the scattering channel to O₃ by Sarpal *et al.* [14] identifies this peak as a manifestation of the shape resonance mechanism. Based on these, it may be possible to assume that the shape resonance mechanism is responsible for most of the observed resonant low-energy inelastic processes in ozone. In addition, the high-resolution measurements of Allan *et al.* [12] have reported a small peak in the O⁻ channel at ~ 0.4 eV, which they attribute to the vertical overlap of the O₃⁻ potential-energy surface (PES) with that of the neutral. However, our calculations [7] have shown that this is not the case, and further information is needed on this peak. The latest, very-high-resolution DEA measurements carried out by the Innsbruck group on O₃ [15] have reported the observation of a very sharp 0 eV peak which vanishes beyond an energy resolution of 100 meV.

In the case of NO₂, apart from qualitative studies of the DEA process [6] and a low-energy total electron cross-section measurement [16], no experimental study on low-energy electron scattering is available. Our measurements show that the three main peaks observed in the O⁻ channel are very similar to that observed for O₃. However, our electron energy resolution is not adequate to resolve the 0.4 eV peak in O₃ or to identify a similar one in the case of NO₂. O⁻ cannot be formed at 0 eV from NO₂ as it is energetically not allowed, so it is only fair to compare the three main peaks from NO₂ with that of O₃. Theoretical or computational work for NO₂ is also sparse. Noting the observed similarities in the DEA signal from NO₂ and O₃, we give below a plausible explanation in terms of a shape resonance mechanism.

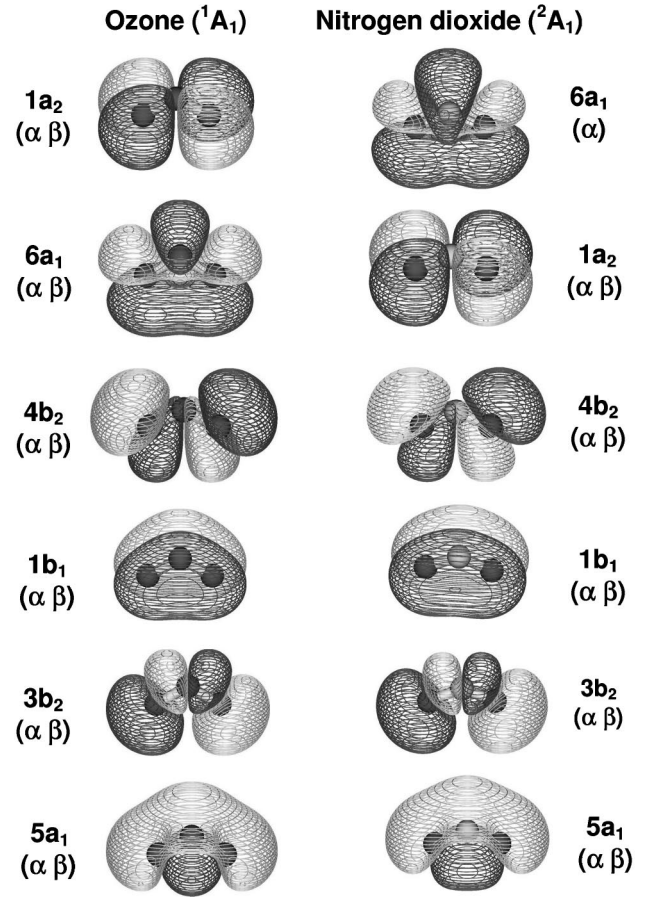
To begin with, we present in Table III a comparison of the relevant parameters important to the electron attachment process. The electron-molecule interaction potential may be written as

TABLE III. Comparison of the experimental (E) and computational (C) numbers of NO_2 and O_3 , relevant to electron capture.

Parameter	NO_2	O_3
Ground-state symmetry	2A_1	1A_1
Bond lengths (\AA)	$d_{\text{N-O}}=1.20$	$d_{\text{O-O}}=1.27$
Bond angles	134°	116.8°
Spatial extent: $\langle r^2 \rangle$ (\AA^2)	30.9	31.3
Dipole moment E : μ (Debye)	0.32 [18]	0.53 [18]
Dipole moment C : μ (Debye)	0.66	0.77
Avg. polarizability E : (\AA^3)	3.02 [19]	3.21 [19]
Avg. polarizability C : (\AA^3)	2.51	2.88, 2.81 [20]
Electron affinity E : (eV)	2.27 [21]	2.10 [21]
Dissociation energy: (eV)	3.11 [19]	1.04 [19]

$$V_{l,l} = \frac{\hbar^2 l(l+1)}{2m_{\text{red}}\rho^2} - \frac{1}{4\pi\epsilon_0} \left(\frac{e\mu \cos\theta}{\rho^2} + \frac{e\alpha(\mathbf{k}, \theta, \phi)}{2\rho^4} \right). \quad (1)$$

In the above expression, ρ is the distance of the electron from the molecular center of mass, the first term represents the angular momentum barrier for orbital angular momentum l , the second term is the interaction of the permanent dipole moment, μ , with the incident electron, and the final term represents the contribution due to the induced dipole moment, i.e., the polarizability, α , which depends on the incident \mathbf{k} vector of the electron and the orientation of the molecule in the space fixed frame denoted by θ and ϕ . The higher-order terms have not been written. This is applicable to shape resonances, and for Feshbach resonances the first term is to be removed, and dipole moments and polarizability suitably altered for core excitation. The fact that these molecules have the same ground-state symmetry and belong to the same point group coupled with comparable sizes, bond lengths, bond angles, and electronic spatial extent $\langle r^2 \rangle$ (see Table III) implies that they project very similar sizes on the incoming electron. The polarizability, dipole moment, and spatial parameters of the NO_2 and O_3 molecules have been calculated at the Møller Plesset (MP) 2 level of approximation with the AUG-cc-pVDZ basis set using the GAUSSIAN 94 [17] package. The spatial parameters provide a measure of the extent of the scattering potential. The mutual agreement in these implies that, in the first term on the right-hand side of Eq. (1), the contribution of the specific angular momentum l will, to a very good approximation, be equal for both O_3 and NO_2 . The experimental dipole moments [18] for these two molecules are somewhat dissimilar, but in both cases very weak. Our computed values of the permanent dipole moment for the two molecules are in better agreement, but higher than the experimentally measured dipole moments, though still weak. The experimentally measured static electric polarizabilities [19] of the two molecules are in excellent agreement with each other. Theoretical values are available only for O_3 [20] and not NO_2 . Our relatively primitive calculations, which are tabulated, are presented to provide a comparison of the NO_2 and O_3 numbers on even terms rather than at different levels of sophistication. They are not intended to supplant the more sophisticated calculations

FIG. 2. Electron density plots for valence orbitals of O_3 and NO_2 .

tions for O_3 . Our computed values of the static polarizabilities for the two molecules agree to within 13% of each other. The computed values of polarizability reported here are the result of the perturbative calculation. In addition, we have also calculated the electron densities of the valence orbitals of both O_3 and NO_2 using the CUBE option of GAUSSIAN 94 at the MP2 level using the same basis set. It can be seen from the density plots, shown in Fig. 2, that the plots are very similar for all the orbitals. The overall shape and density would be the same for the two molecules except for the additional β electron in the $6a_1$ orbital of O_3 , which will not change the overall shape. Thus the charge distribution seen by the incoming electron is very similar. This, coupled with the fact that the polarizabilities are very similar, would lead to an almost identical electron-molecule interaction potential, leading to similar eigenstates and hence similar resonances. Based on this, one may expect to see similar electron attachment channels in both NO_2 and O_3 , which may explain the observed similarity in the DEA cross sections. An extension of this explanation may lead us to conclude that the observed resonances in the DEA of NO_2 may also be shape resonances similar to those in O_3 , based on the available evidence that the resonances in O_3 have mostly been assigned as shape resonances. In this context, it may be appropriate to cite the recent theoretical work on electron scattering on NO_2 by Curik *et al.* [22]. They have calculated the

integral elastic electron scattering cross sections and have discussed the spatial shapes of their low-energy single-particle resonances. They show the feasibility of interpreting the dissociative attachment data in terms of the spatial shapes of the single-particle resonances and their similarities to the electron- O_3 scattering.

It is appropriate that we also discuss the limitations of the model given above, for the sake of completeness. To begin with, the data from the two molecules are not entirely identical, the major difference being in the magnitude of the cross sections. Though the ion yield curves show very close similarity, the absolute cross sections differ by about a factor of 4 for these molecules. This difference may be explained from the fact that despite the similarity in the formation of the resonances, the data pertains to the DEA process, where the competing processes of electron detachment and molecular dissociation could give rise to the observed difference in the magnitude of the cross sections. It is well known that the DEA cross section is very sensitive to the changes in internuclear separation as well as the crossing point of the potential-energy curves of the negative ion resonance and the neutral molecule. The observed difference may be qualitatively explained based on these as given below.

The DEA cross section σ_{DA} can be written as the product of the cross section σ_c for the electron capture resulting in the formation of the negative ion resonance and the “survival probability,” p , i.e., the probability that the negative ion resonance will decay by dissociation,

$$\sigma_{DA}(E) = \sigma_c(E)p(E), \quad (2)$$

where E represents the incident electron energy. The capture cross section σ_c depends on the symmetry properties of the neutral molecule and the negative ion resonance and their Franck-Condon overlap. p depends on the mean lifetime of the resonance due to autodetachment and the separation time of the dissociation fragments. Thus the dissociative attachment cross section is strongly dependent on the competition between the two modes of decay of the resonance, viz., autodetachment and dissociation. The survival probability, against autodetachment, can be explicitly written as [23–26]

$$p(E) = \exp\left(-\int_{R_E}^{R_c} \frac{\Gamma_a(R)}{\hbar v(R)} dR\right) \approx \exp\left(-\frac{\tau_s}{\tau_a}\right), \quad (3)$$

where Γ_a is the autodetachment width, R_E is the internuclear separation at which the electron is captured, R_c is the internuclear separation beyond which autodetachment is not possible, and $v(R)$ is the relative velocity of separation of the dissociating fragments. τ_s is the time needed for AB^{-*} to separate from R_E to R_c given by

$$\tau_s = \int_{R_E}^{R_c} \frac{dR}{v(R)} \quad (4)$$

and

$$\bar{\tau}_a = \frac{\hbar}{\Gamma_a} \quad (5)$$

is the mean autodetachment lifetime of AB^{-*} with $\bar{\Gamma}_a$ being the average autodetachment width.

From the expression for $p(E)$ [Eq. (3)] it is evident that as R_E becomes closer to R_c , τ_s decreases and $p(E)$ increases exponentially. From Table III it can be seen that the bond distance in the case of NO_2 is 1.2 Å, whereas that for O_3 is 1.27 Å. Thus assuming everything else is similar to both systems, the DEA cross section for O_3 should be larger. Moreover, the bond dissociation energy for NO_2 is 3.1 eV, whereas that for O_3 is only 1 eV. Based on this, the distance between R_c and R_E for the case of O_3 should be considerably closer as compared to that for NO_2 . This again should lead to a larger DEA cross section for O_3 . It is difficult to evaluate these cross sections based on the presently available theoretical predictions. But it is obvious that absolute cross sections will be very sensitive to the finer differences in the two molecules. Moreover, the difference in the cross sections is in the right direction as expected from the difference in the internuclear separations and the dissociation energies. Thus the observed difference in the absolute cross sections may not be held against our suggestion of a common behavior in the capture process.

In the above model, we have assumed shape resonance mechanism to be dominant in the resonance attachment. However, it is possible that core excited shape resonances and Feshbach resonances may contribute, particularly at higher energies. In these cases the excited states of the neutral molecules become important. The question that arises is whether the excited states of NO_2 and O_3 have similar energies. Considering the fairly large density of states in these molecules, it may not be difficult to find matching energy levels. This is an important question to be addressed theoretically in order to make a definite conclusion from the model we have presented. Also, it is necessary to have calculations on the entire dissociative attachment process, which takes into account not only the competition between the autodetachment decay and the dissociation, but also the competition between the various channels of dissociation in the triatomic system in order to have a firm understanding of the observed results. In the meanwhile, it remains an intriguing question whether the DEA and related low-energy resonant electron capture processes need to be studied in isolation for different molecules, or whether molecular species can be found where the electron capture part of the phenomenon can arguably be treated on a common footing. Given the fact that theoretical/computational methods have significant challenges ahead of them, such similarities between molecules may aid in parametrizing the problem in more general terms.

IV. CONCLUSIONS

Absolute cross sections for the formation of O^- from NO_2 by dissociative electron attachment have been measured. The data show remarkable similarity to the formation of O^- from O_3 by the same process. This *a priori* unexpected similarity has been interpreted as due to an almost

identical electron-molecule potential arising from the very similar geometric and electric properties of the two molecules. Such a common behavior in resonant electron capture to molecules that are not isoelectronically related has not been commented on in the literature.

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- [1] Ch. K. Kwan, Y.-F. Hsieh, W. E. Kauppila, S. J. Smith, T. S. Stein, M. N. Uddin, and M. S. Dababneh, *Phys. Rev. Lett.* **52**, 1417 (1984).
 - [2] G. J. Schulz, in *Principles of Laser Plasmas*, edited by G. Bekefi (Wiley, New York, 1976), Chap. 2.
 - [3] J. E. Turner, *Am. J. Phys.* **45**, 758 (1977).
 - [4] W. Domcke, *Phys. Rep.* **208**, 97 (1991).
 - [5] J. A. D. Stockdale, R. N. Compton, R. N. Hurst, and P. W. Reinhardt, *J. Chem. Phys.* **50**, 2176 (1969).
 - [6] R. Abouaf, R. Paineau, and F. Fiquet-Fayard, *J. Phys. B* **9**, 303 (1976).
 - [7] S. A. Rangwala, S. V. K. Kumar, E. Krishnakumar, and N. J. Mason, *J. Phys. B* **32**, 3795 (1999).
 - [8] E. Krishnakumar, S. V. K. Kumar, S. A. Rangwala, and S. K. Mitra, *Phys. Rev. A* **56**, 1945 (1997).
 - [9] S. K. Srivastava, A. Chutjian, and S. Trajmar, *J. Chem. Phys.* **63**, 2659 (1975).
 - [10] D. Rapp and D. D. Briglia, *J. Chem. Phys.* **43**, 1480 (1965).
 - [11] L. G. Christophorou, D. L. McCorkle, and A. A. Christodoulides, in *Electron Molecule Interactions and Their Applications*, Vol. 1, edited by L. G. Christophorou (Academic Press, Orlando, 1984), Chap. 6.
 - [12] M. Allan, K. R. Asmis, D. B. Popovic, M. Stepanovic, N. J. Mason, and J. A. Davies, *J. Phys. B* **29**, 4727 (1996).
 - [13] B. Nestmann (private communication).
 - [14] B. K. Sarpal, B. Nestmann, and S. D. Peyerimhoff, *J. Phys. B* **31**, 1333 (1998).
 - [15] G. Senn, J. D. Skalny, A. Stamatovic, N. J. Mason, P. Scheier, and T. D. Märk, *Phys. Rev. Lett.* **82**, 5028 (1999).
 - [16] C. Szmytkowski, K. Maciąg, and A. M. Krzysztofowicz, *Chem. Phys. Lett.* **190**, 141 (1992).
 - [17] GAUSSIAN 94, Revision C.2, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople (Gaussian, Inc., Pittsburgh, PA, 1995).
 - [18] D. R. Lide, in *CRC Handbook of Chemistry and Physics*, 76th ed., edited by D. R. Lide (CRC, Boca Raton, FL, 1995–1996), pp. 9–42.
 - [19] T. M. Miller, in *CRC Handbook of Chemistry and Physics* (Ref. [18]), pp. 10–192.
 - [20] G. Maroulis, *J. Chem. Phys.* **101**, 4949 (1994).
 - [21] S. V. Khristenko, A. I. Maslov, and V. P. Shevlelko, *Molecules and Their Spectroscopic Properties*, Springer Series in Atoms and Plasmas (Springer, Berlin, 1998), Chap. 4.
 - [22] R. Curik, F. A. Gianturco, R. R. Lucchese, and N. Sanna, *J. Phys. B* **34**, 59 (2001).
 - [23] T. F. O'Malley, *Phys. Rev.* **150**, 14 (1966).
 - [24] J. N. Bardsley, A. Herzenberg, and F. Mandl, in *Atomic Collision Processes*, edited by M. R. C. McDowell (North-Holland, Amsterdam, 1964), pp. 415–427.
 - [25] J. N. Bardsley, A. Herzenberg, and F. Mandl, *Proc. Phys. Soc. London* **89**, 321 (1966).
 - [26] J. C. Y. Chen, *Phys. Rev.* **148**, 66 (1966).