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HAL Id: hal-04753094

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Production of nitrogen dioxide, NO₂⁻, anion from dissociative electron attachment to nitromethane below 1 eV and its temperature dependence

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ABSTRACT

Reaction induced by slow electrons is implicated in a large field of research and application. At these energies, the electron attachment that efficiently fragments molecules, is usually initiated via (1) shape resonance, or (2) mediated by the formation of a dipole bound anion. While the temperature dependence of (1) is well known, that of (2) is not clearly established. Nitromethane is the prototypical molecule for which the electron attachment leads to the formation of both a dipole bound and a covalent anion. We provide here a comprehensive study of the fragmentation of nitromethane by < 1 eV electron and the unusual temperature effects attributed principally to process (2).

The ubiquitous role of low energy electrons in a large field of research and application has been demonstrated [1] and the fundamental of their interaction with molecules is now well understood [1,2,3]. In brief, the colliding electron is captured by the target molecule to form a transitory negative ion which may (1) be stabilized to form a long-lived anion, (2) eject the extra electron (auto-ionization) or, (3) dissociate into a negative ion and one or more neutral counterpart(s), this last channel is also known as Dissociative Electron Attachment (DEA). At electron energies below the electronic excitation of molecules (i.e., typically ~3-4 eV), this transitory precursor anion usually arises from the accommodation of the electron in an unoccupied molecular orbital via shape resonance; at higher energies, the excitation of a valence electron concomitantly to the capture of the incoming electron (i.e., two particles-one hole) is implicated for the formation of the parent anion. At much lower energies (<100 meV), the negative parent anion may be formed by the binding of the excess electron due to the long-range electrostatic potential of the molecule, e.g., via the dipole moment of the molecule as a dipole bound (DB) anion [4,5,6]. As for the shape resonance the extra electron occupies an empty valence orbital, in the dipole bound anion, the electron is localized outside the molecular frame. However, the DB state may couple to the valence state for the formation of a precursor anion [7,8]. In this process, the colliding electron trapped by the molecular dipole field in a dipole bound state may transfer some energy to vibrationally excite the target molecule, before being transferred into a valence state as it has been suggested in DEA to uracil experiments [7]. For DEA via shape or core excited resonance, the temperature effect is well known theoretically [1-3] and documented experimentally [9]. In contrast, this effect is still not elucidated in the case of DEA mediated by the formation of a dipole bound anion.

Nitromethane (CH_3NO_2) is the prototypical molecule that exhibits this DB to valence state coupling. It has been shown that DB anion can be formed [10] from the transfer of electron in the collision of laser excited Rydberg Xe atom to cold nitromethane produced in supersonic expansion. Indeed, the dipole moment of CH_3NO_2 (c.a., 3.46 D) is well above the critical dipole moment for the formation of a DB anion [4,6], and the binding energy, BE_{DB} , of the extra electron to nitromethane has been measured to be 15 meV [6,10]. In this collision experiment, the excess energy in the dipole bound anion is stabilized by the Rydberg Xe^+ positive core. At low temperature, it has also been reported that the valence anion [10,11] is mediated by the change in the geometry of the nitromethane, i.e., out-of-plane rotational or wagging motion of the nitrogen dioxide, NO_2 , group (Figure 1). In collision of free low energy electrons with room temperature nitromethane molecules, the results differ [12,13]. Indeed, no precursor, CH_3NO_2^-

anion is observed in contrast to the Rydberg electron transfer experiments. Instead, it is the NO_2^- anion fragment that is observed at electron energies below 2 eV.

In this Letter, we study theoretically and experimentally the collision of free low energy (< 2 eV) electrons with nitromethane targets and the temperature effects in the production of the NO_2^- anion fragments, when the nitromethane is thermally heated prior to the collision. Calculations with the Gaussian16 suite of programs [14] have been performed in the framework of the density-functional theory (DFT) and its time-dependent formalism (TDDFT) using the aug-cc-pvtz basis set [15] and the ωB97x exchange-correlation functional [16]. This level of calculations has been recently showed to be reliable to describe the electron attachment [17,18]. From the experimental side, the molecular vapor is injected through a stainless steel capillary which is encapsulated in a brass sheath that can be resistively heated. The molecular beam crosses at right angle an electron beam of 0.24 eV energy resolution provided by a trochoidal monochromator, and the produced ions are detected by a time-of-flight mass spectrometer: this equipment is maintained at room temperature [19]. During the measurements the pressure in the collision chamber is constant (c.a., $1.4 (\pm 0.2) 10^{-6}$ mb). The molecular beam consists of pure nitromethane or an admixture of CH_3NO_2 and carbon tetrachloride (CCl_4). The use of CCl_4 permits the energy calibration of the electrons and the evaluation of the ion production cross section [19]. At a given collision energy, we measure the number of produced negative ions which is thereafter normalized by the measured electron current: thus, this anion yield is only parametrized by the electron energy and temperature of the molecular beam.

Figure 2A presents the anion mass spectra recorded at the electron energy of 0.4 eV. The solid line is obtained from the electron impact to pure beam of nitromethane while the dashed line, to the $\text{CH}_3\text{NO}_2\text{-CCl}_4$ admixture. As it can be seen, only NO_2^- anion fragment is observed (at m/z 46), in addition to the Cl^- anion for the admixture gas. The NO_2^- anion yield function, shown in Fig. 2B, indicates a peak corresponding to the anion fragment production at 0.55 eV in agreement with the 0.6 eV reported elsewhere [12,13]. This peak position is supported by our calculations that determined the anionic state to be lying at 0.54 eV above the neutral molecule in a vertical process. Figure 3A presents the calculated potential energy curves (PECs) of the neutral molecule (purple, PEC_N), the anion (black, PEC_A1) as the function of the C-N bond elongation. The red PEC (PEC_A2), obtained after relaxing the anion at each C-N bond distance, is below the PEC_N. The minimum of the PEC_A1 lies at 0.54 eV above that of the PEC_N. To dissociate, a potential barrier of about 1 eV must be overcome. Therefore, the fragmentation for the NO_2^- anion cannot arise along this PEC_A1, i.e., keeping the geometry

of the neutral molecule. Alternatively, as the extra electron attached to the molecule, the wagging energy of 0.32 eV is sufficient for the molecule to change the geometry via the out-of-plane rotation of the O atoms. For a totally relaxed anion, the PEC_A2 does not cross the PEC_N, however it is possible that the crossing arises at some degrees of relaxation, as shown in Figure 3A. After the capture of the extra electron, the dominant geometric changes are: first, an increase of the NO₂ tilt angle together with the rotation of the CH₃, and then an elongation of the C-N bond. The fragmentation probability depends on the coupling matrix elements and the slopes of the intersecting PECs (i.e., Landau-Zener probability, LZP [20]). The last possible dissociation channel, which cannot be ruled out, is associated to the dissociation mediated by the formation of a dipole bound anion [8]. The potential energy curve of the dipole bound anion as the function of the C-N bond distance is obtained by shifting the PEC_N by the DB binding energy, c.a., 15 meV [6,9] (dashed purple line, Fig.3B) and, the dissociation probability is also controlled by LZP. Nonetheless, the potential barrier must be overcome for the fragmentation. Therefore, the fragmentation probability, or the anion signal, must be a convolution of the LZP and the barrier transmission probability. It is to be noted that for the electron attachment near 0 eV, the analysis of our PECs (purple and grey lines, Fig.3) indicates that the electron attachment via the formation of a dipole bound anion following by the coupling of this state with a valence state would lead to the formation of a stable CH₃NO₂⁻ anion, as observed in the Rydberg electron transfer experiments [10], since the high potential barrier of the anion PEC to overcome. This analysis agrees well with Sommerfeld's model [8].

The heating of the molecular beam leads to the ro-vibrational excitation of the molecule. In the present experiment, the heating temperature is at most 393 K corresponding to an excitation energy of 33.86 meV (i.e., 273.1 cm⁻¹). Only few vibrational modes are affected (**SI1**), those modes do not affect the NO₂ group since the NO₂ wagging and the C-N stretching modes are too high in energy to be accessible (i.e., 640, 686, 968 cm⁻¹, and higher, see **SI2**). The calculated Gibbs free energies (Table 1) for the fragmentation predict a strong lowering of the barrier and the fragmentation becomes accessible at room temperature. Thus, the transmission probability is expected to increase as the temperature increases, i.e., from 290 K to 390 K, resulting in an increase in the NO₂⁻ anion signal in agreement with the already known results from temperature dependence of DEA via shape resonance [3,9]. Yet, the temperature dependence of the NO₂⁻ anion produced from the impact of 0.7 eV electron, exhibited in Figure 4, shows an unexpected decrease in the fragment yield. This behavior has been reported for low energy impact on

thiothymine and chlorotoluene experiments [21,22], for which the mechanism has not been fully understood and confirmed theoretically.

For the DB mediated DEA, as for DEA via shape resonance, the LZP strongly depends on the DB potential energy curve, i.e., the EB_DB value that shifts the PEC_N (dashed line, Fig. 3B), as mentioned above. The binding energy in a symmetry top DB anion is well described in the framework of the Clary's model [23], and additional terms related to the rotational states of the molecule have to be included. As the dipole bound anion of nitromethane can be treated within the prolate symmetry top Clary's model [6,22] (i.e., rotor constants of the molecule to be 12.54508 GHz, 10.68212 GHz and 5.98631 GHz from our calculations), the EB_DB can be estimated to $-15 \text{ meV} + bJ(J+1) + (a-b)k^2$ [23], a and b being the rotor constant of the symmetry-top molecule, and J and k the quantum numbers associated to the \mathbf{J}^2 rotational angular momentum operator of the molecule and its projection along the symmetry axis \mathbf{J}_z . Thus, EB_DB vanishes for a (J,k) set of high values so that the electron will no longer be bound as a DB anion. From the Clary's model applied to nitromethane, the highest J value for which the DB anion is still formed, is found to be $J_{\text{max}} = 16$ ($k = 0$) with a EB_DB of about 1 meV (**SI3**). This is also in agreement with the Garrett's theory on the rotational auto-detachment of dipole-bound anion [24,25]. This maximum accessible J value has to be compared to the most probable J values for T=293 K and 393 K, estimated by the Boltzmann partition function of the populated rotational states, which are found to be 22 and 25, respectively (**SI4**). From the analysis of the partition function, it is then clearly seen that the total probability for populating the rotational states up to $J = 16$ decreases as the temperature increases. Furthermore, the ratios bound/unbound states are found to be 31% (T=293 K) and 19.5% (T=393 K), calculated for $k = 0$. Thus, for the DB mediated DEA, the total dissociation probability, which must be a contribution of each accessible (J,k) state with the LZP being weighted by the partition function of the associated rotational state, must decrease as the temperature increases. Nevertheless, the estimated trend based on the Boltzmann rotational partition function can support to some extent the decrease in the NO_2^- anion production reported in Fig. 4. It is to be noted that the temperature effect on the formation of the dipole bound anion depend also on the rotor constants of the molecule: small temperature range for high rotor constant values. For nitromethane, the rotor constant is much higher than that of thiothymine [21], thus the temperature range is found to be smaller here (i.e., 300-380 K, Fig. 4) than for the larger molecule (i.e., up to 450 K).

In this Letter, we provide a comprehensive discussion on the fragmentation of nitromethane by $< 1 \text{ eV}$ free electron for the production of the NO_2^- anion and the formation of

a long lived CH_3NO_2^- anion in the Rydberg electron transfer technique [10]. For the transitory parent anion fragmentation, two competitive processes, i.e., DEA via (1) shape resonance and (2) mediated by the formation of a dipole bound anion may be, a priori, both implicated. While the temperature dependence of (1) is well known, i.e., the dissociation cross-section (i.e., formation of anion fragment yield) increases with the heating temperature [3,20], the temperature effect of (2) is yet unestablished in such a detail. From the measurements and the support of theory, we suggest that an increase of the rotational level of the molecule, due to an increase of the molecule temperature, disfavors the binding of the extra electron in the dipole bound state, consequently, the process (2). Nonetheless, we cannot rule out some contributions of process (1), which might not be predominant for nitromethane at temperature < 300 K, but still exist at higher temperature.

SUPPORTING INFORMATION

SI1: Adiabatic avoided crossing between nitromethane dipole-bound state and the valence state evaluated with DFT/TD-DFT with (3sp)-aug-cc-pvtz basis set and ω B97x exchange-correlation functional.

SI2: Harmonic frequencies (cm^{-1}) calculated at ω B97x/aug-cc-pvtz level.

SI3: Dipole bound binding energy estimated using Clary's model.

SI4: Partition function of the populated rotational states.

ACKNOWLEDGMENTS

This study was supported by the ANR-PRC-BAMBI program (grant number 18-CE30-0009-03). In addition, G.T. and F.R. thank the GENCI-IDRIS for supporting the computing time through the grant A0150807662.

TABLES

Table 1: Gibbs free energies of fragmentation and reactions resulting in the production of NO_2^- calculated at the ω B97x/aug-cc-pvtz level at 0, 290, 390 K.

Reaction	Gibbs Energy (eV)		
	T = 0 K	T = 290 K	T = 390 K
$\text{CH}_3\text{NO}_2 + e^- \rightarrow \text{CH}_3 + \text{NO}_2^-$	0.66	-0.07	-0.24

FIGURES

FIGURE 1: Structure of the nitromethane molecule (a) and its anion (b). The molecular orbital occupied by the extra electron in the dipole bound state (c) and the valence anion state (d).

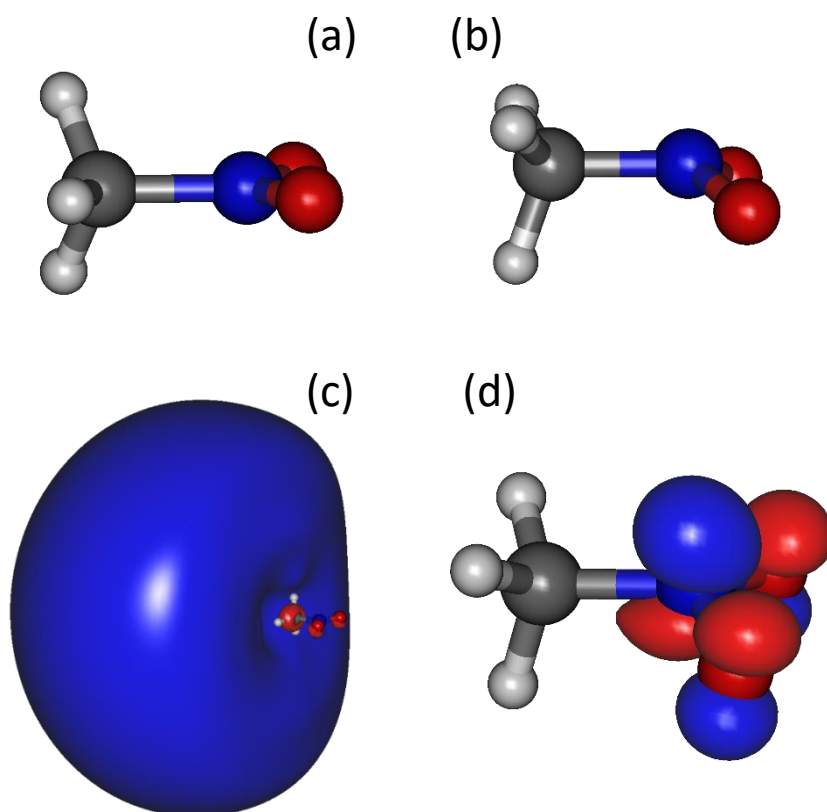
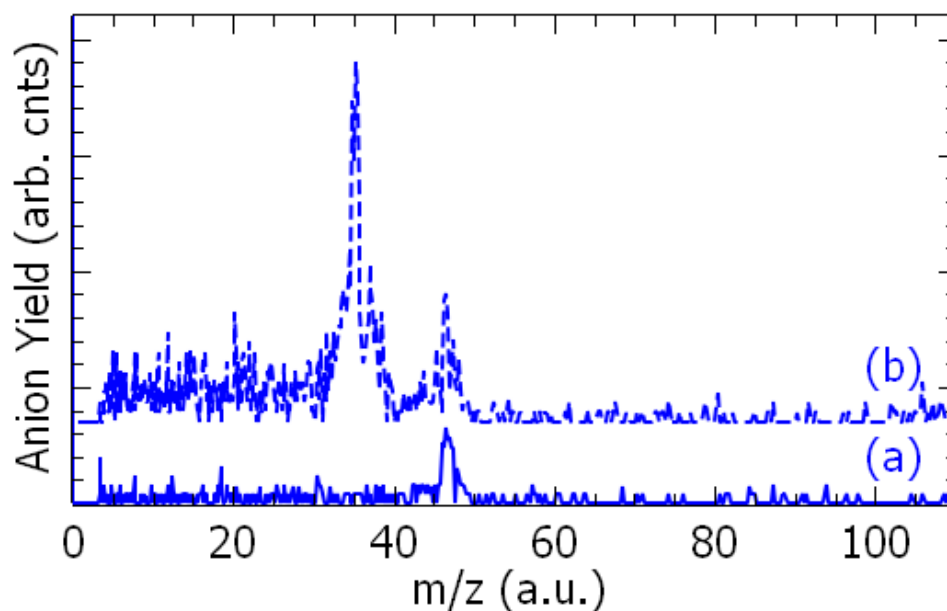


FIGURE 2: (A) Anion mass spectra recorded at 0.4 eV electron energy from (solid line, a) pure nitromethane beam, (dashed line, b) admixture of nitromethane and carbon tetrachloride (for calibration).



(B) Yield of the NO_2^- anion as the function of the incident electron energy (eV). The yield function is recorded (a) at room temperature 300 K and, (b) at 373 K. The anion yields are normalized by the electron current.

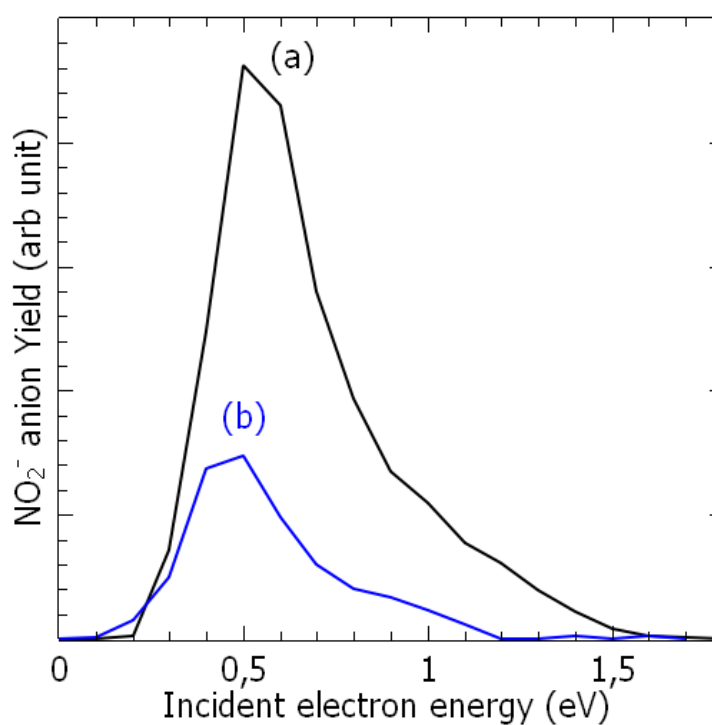
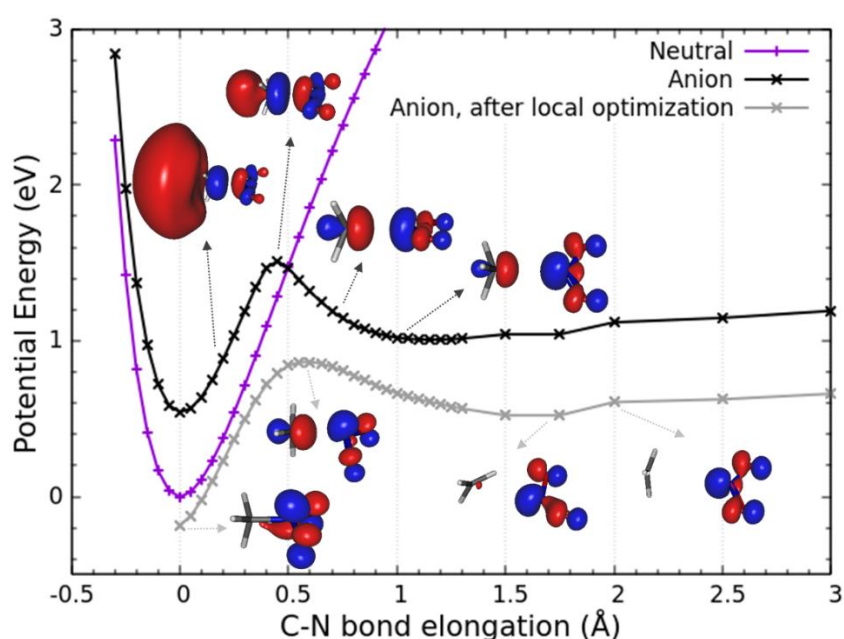


FIGURE 3: (A) Potential Energy Curves (PECs) as the function of the C-N elongation. PEC of the neutral molecule (purple line), the anion at the geometry of the neutral (black line) and the anion for which the structure is relaxed for each C-N position (grey line). The orbital occupied by the extra electron is also shown. In the case of vertical attachment (black line), the electron, initially in a dipole bound state, occupies an orbital with a mixed character (long-range and covalent) for $d < 0.5$, the charge is gradually transferred to NO₂ part for $d > 0.5$ in a antibonding dissociative state. In contrast, when the structure is locally relaxed (grey line), the electron is located on the NO₂ part at $d = 0$ thanks to out-of-plane rotational motion of the NO₂ group. While increasing d , the CH₃ part tends to become planar and a partial electron charge is found on CH₃. For $d > 0.6$, the electron is mainly localized on NO₂.



(B) Potential Energy along the neutral to anion transit; i.e. the local optimization of the anion starting from the neutral structure. After the capture of the extra electron, the dominant geometric changes are an increase of the NO₂ tilt angle together with the rotation of the CH₃, then an elongation of the C-N bond. The dashed line represents the dipole bound anion PEC, consisting of a shift of the neutral PEC by the electron binding energy of 15 meV (see text). Here, the energy of the valence anion is underestimated owing to a partial relaxation of the anion (particularly, CH₃ is kept as it is in the molecule instead of becoming planar). The adiabatic avoided crossing between dipole bound and valence anionic states is shown in Fig.3A.

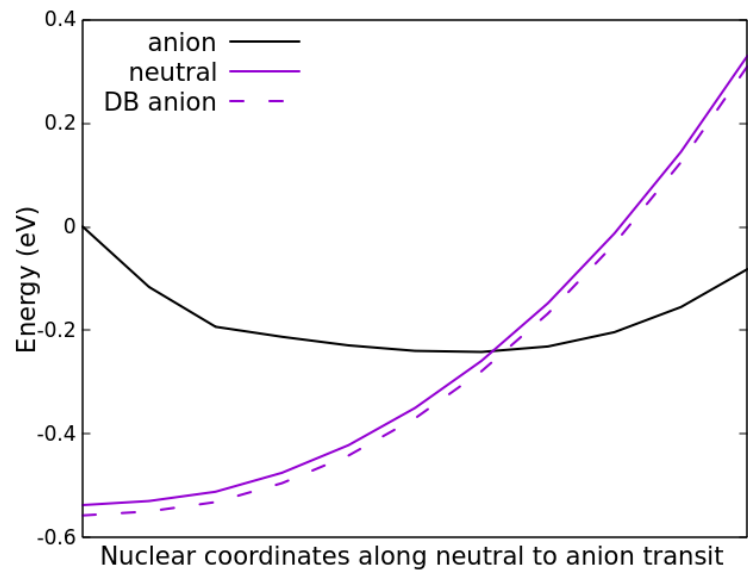
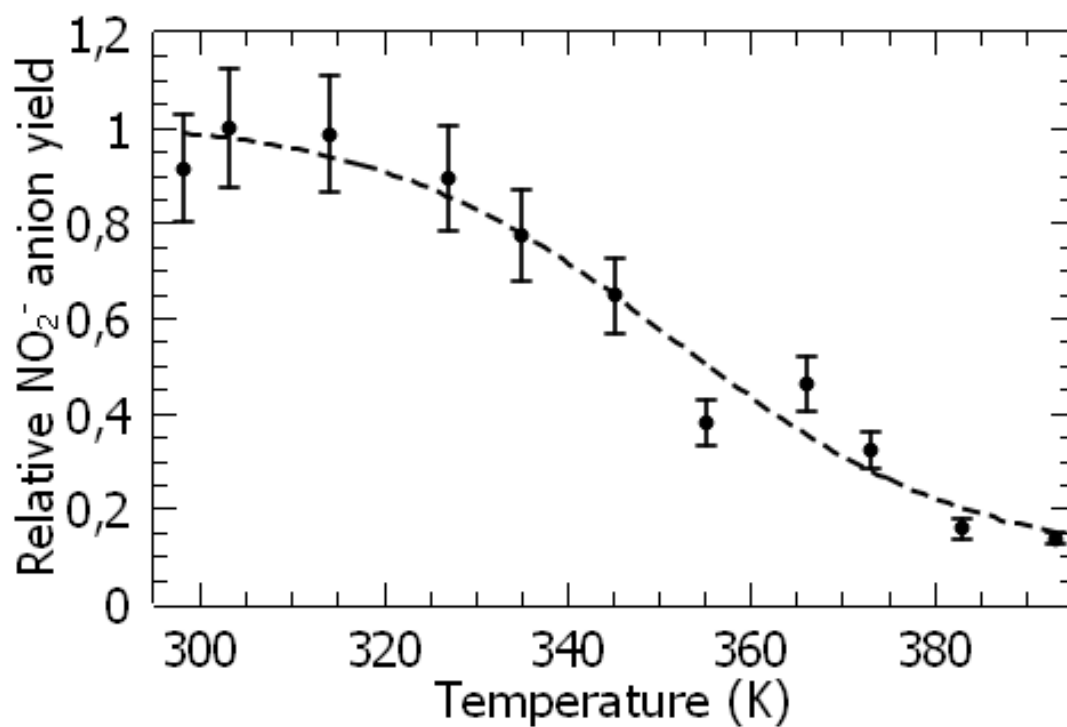


FIGURE 4: Relative NO_2^- anion yield, produced from the impact of 0.7 eV electron, as the function of the gas heating temperature. Each point is obtained by averaging five measurements. The error bars are estimated to be 25% and, the temperature (ΔT) is 3K. The dashed line is a guide-to-the-eye.



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Production of nitrogen dioxide, NO_2^- , anion from dissociative electron attachment to nitromethane and its temperature dependence

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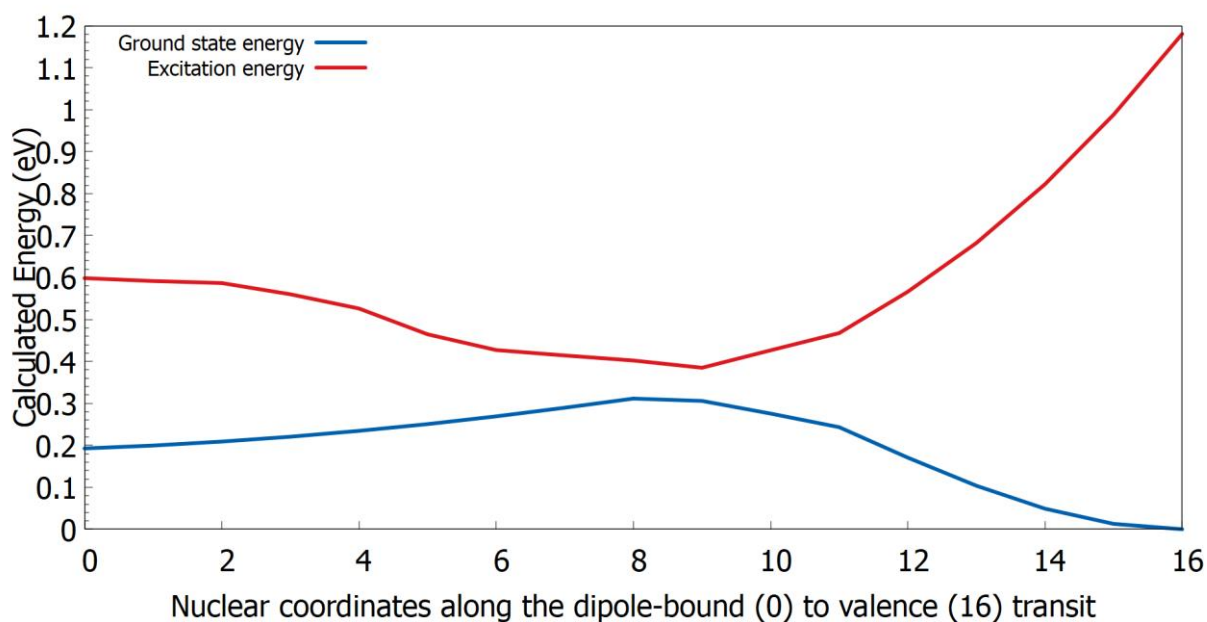
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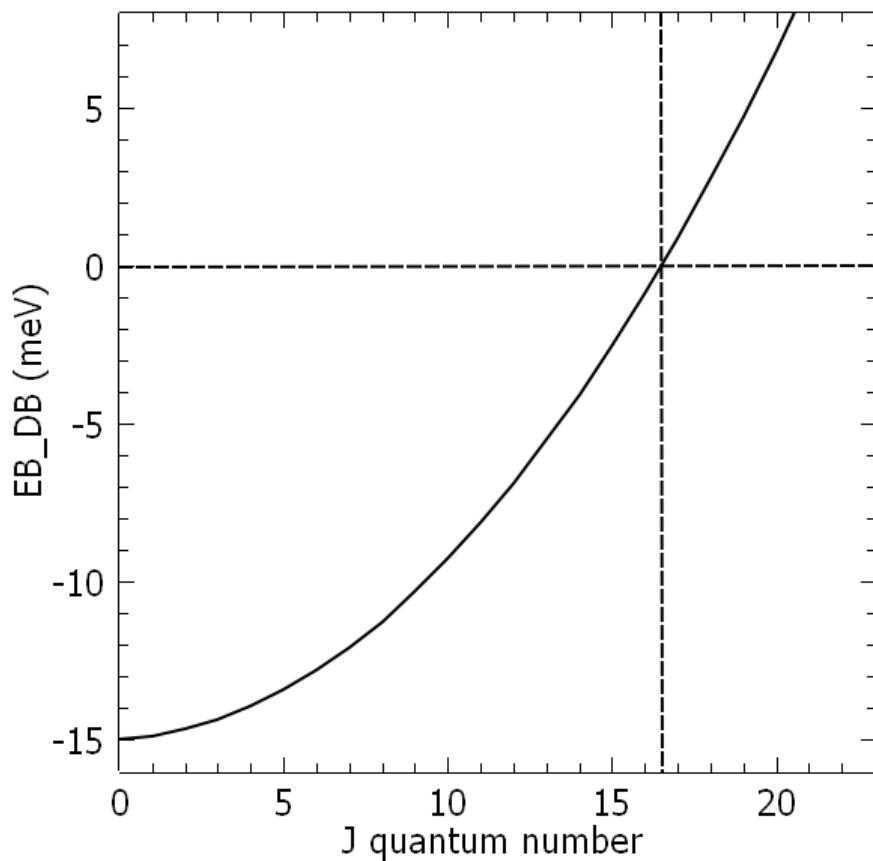
SI1: Adiabatic avoided crossing between nitromethane dipole-bound state (on the left-hand side) and the valence state (on the right-hand side) evaluated with DFT/TD-DFT with (3sp)-aug-cc-pvtz basis set and ω B97x exchange-correlation functional. Details on the construction of the basis set can be found in Ref [G. Thiam, F. Rabilloud, How accurately can DFT describe non-valence anions ?, *J. Chem. Theory Comput.*, 19, 2842-2849 (2023)]. Intermediate geometries between the geometry of the dipole-bound anion and the valence anion have been generated by linear interpolation of the atomic positions between the two initial and final geometries.



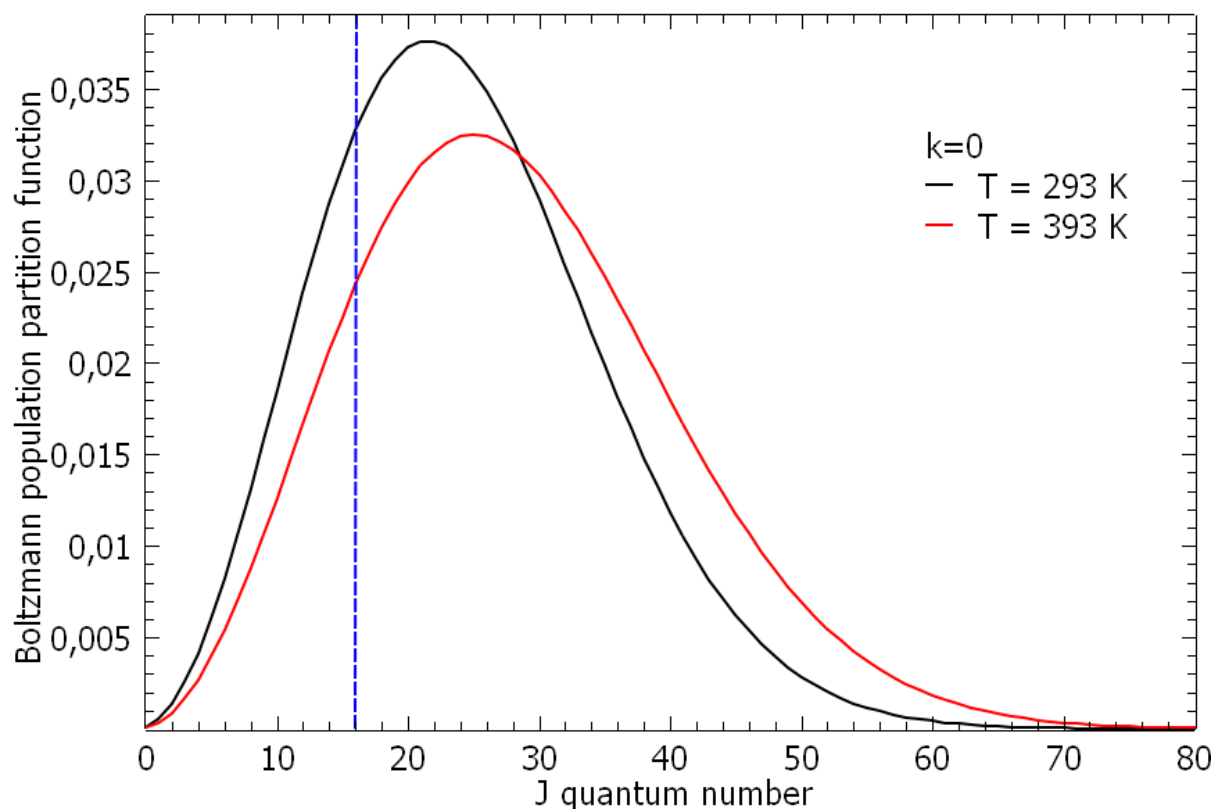
SI2: Harmonic frequencies (cm^{-1}) calculated at $\omega\text{B97x/aug-cc-pvtz}$ level.

17.6076	492.7165	640.2440
686.3074	968.8646	1123.2186
1153.2579	1424.6497	1469.4344
1484.8525	1502.2195	1697.6456
3115.4127	3213.9011	3240.0392

SI3: Electron binding energy in dipole bound anion, EB_DB, estimated by Clary's model [1]: $EB_DB = -15 \text{ meV} + bJ.(J+1) + (a-b)k^2$, calculated here for $k=0$. The dashed lines correspond to the J value for a binding energy of 0 eV: $J_{\text{max}} = 16$ represents the last accessible DB bound state.



SI4: The partition function of a (J,k) rotational state are populated via $\varpi_{J,k} = P_J \cdot P_k / (s \cdot Q)$, with s, Q, and P_J and P_k being, respectively, the symmetry number [2], rotational partition function, and the Boltzmann distributions ($P_J = (2J+1) \exp(-bJ(J+1)/k_B T)$ and $P_k = \exp(-(a-b)k^2/k_B T)$, k_B the Boltzmann constant) [3]. Thus, the statistical population in a specific J state can be obtained by summing all accessible k states, $\varpi_J = \sum_k \varpi_{J,k}$. The dashed blue line indicate $J = 16$, for which the electron binding energy in a DB anion is ~ 1 meV.



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