Reply to: The stabilization of cyanonaphthalene by fast radiative cooling

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In our original article[1], we found that the dissociation of an ensemble of vibrationally hot 1-cyanonaphthalene cations (1-CNN⁺, $C_{10}H_7CN^+$) was quenched by radiative cooling after a time corresponding to a critical rate coefficient $k_c = 300(20) \, s^{-1}$. This is much higher than can be attributed to vibrational cooling through the emission of infrared photons ($k_{IR} < 100 \, s^{-1}$). It is also much higher than can be explained by recurrent fluorescence—optical photon emission from thermally excited electronic states—if Herzberg–Teller coupling is not included in the calculation of the oscillator strength of the electronic transitions involved. This efficient radiative stabilization closes some of the dissociation channels included in current astrochemical models, which underpredict the abundance of 1-CNN in the molecular cloud TMC-1 by six orders of magnitude[2]. In his Matters Arising comment, Professor Hansen suggests an alternate interpretation of our experimental observables, which implies a higher activation energy for the dissociation of 1-CNN⁺. It does not, however, alter the essence of the conclusions of our original article.

The so-called Finite–Heat–Bath (FHB) theory is required to reconcile the concepts of energy and temperature in isolated molecules and clusters. For a single molecule, the internal excitation energy E is well-defined and conserved. The "temperature" T of such a system is that of a fictitious ensemble, with Botzmann-distributed excitation energies[3], and with an average energy equal to E. For unimolecular reactions, FHB theory equates the microcanonical expression for the rate coefficient k connecting reactant to products with the classical Arrhenius law:

$$k = A \frac{\rho(E - E_a)}{\rho(E)} = A e^{-E_a/k_B T_{eff}},\tag{1}$$

where A is a constant, ρ is the density of excited states of the system, and E_a is the activation energy of the reaction[4]. The question arises, given that E is the energy of the reactant, what is the ensemble characterized by temperature T_{eff} that makes the above equation correct? As laid out by Hansen in his comment, it is not that of the reactant or the product, but of what he refers to as "the decaying molecule." This temperature may be estimated by a Taylor expansion of the state densities in Eq. (1) and is given to first order in E_a by

$$T_{eff} \approx T_{prod} + \frac{E_a}{2C} \approx T_{reac} - \frac{E_a}{2C},\tag{2}$$

where T_{prod} and T_{reac} are the temperatures of the product and reactant, respectively, and the heat capacity C is assumed to be the same for the product and reactant, and independent of temperature[4].

In our original article[1], we analyze our measured kinetic energy release (KER) distributions in the framework of RRKM theory using expressions derived by Hansen[5] from the standard RRKM model of the rate coefficient. As acknowledged by Hansen in his comment, the temperatures extracted from this analysis pertain to the transition state. However, Hansen argues that, given the small reverse reaction barrier (6.2(5) meV) determined from the KER distributions, the temperature of the transition state $T^\ddagger$ is equal to T_{prod}. In our analysis, we instead identify $T^\ddagger$ with the temperature T_{eff} of "the decaying molecule". We find this interpretation more suitable, as the transition state of a unimolecular dissociation reaction is usually defined as the plane in phase space separating reactants from products, i.e. "the decaying molecule". We note that FHB theory has mainly been used to explain the evaporation rates of non-covalent clusters and thermionic emission, which, unlike chemical bond-breaking, lack well-defined transition states, and where the state densities and heat capacities are similar for the reactant and product[4,6].

However, for the sake of argument, we will hear Hansen's suggestion concerning the effective temperature and re-analyze our time-dependent KER distributions assuming that $T^\ddagger = T_{prod}$, i.e. replacing Eq. 8 in [1] by:

$$k_{diss}(E(T^\ddagger)) \approx \frac{k_B T^\ddagger}{h} e^{-E_a'/k_B[T^\ddagger + E_a'/2C]}.\tag{3}$$

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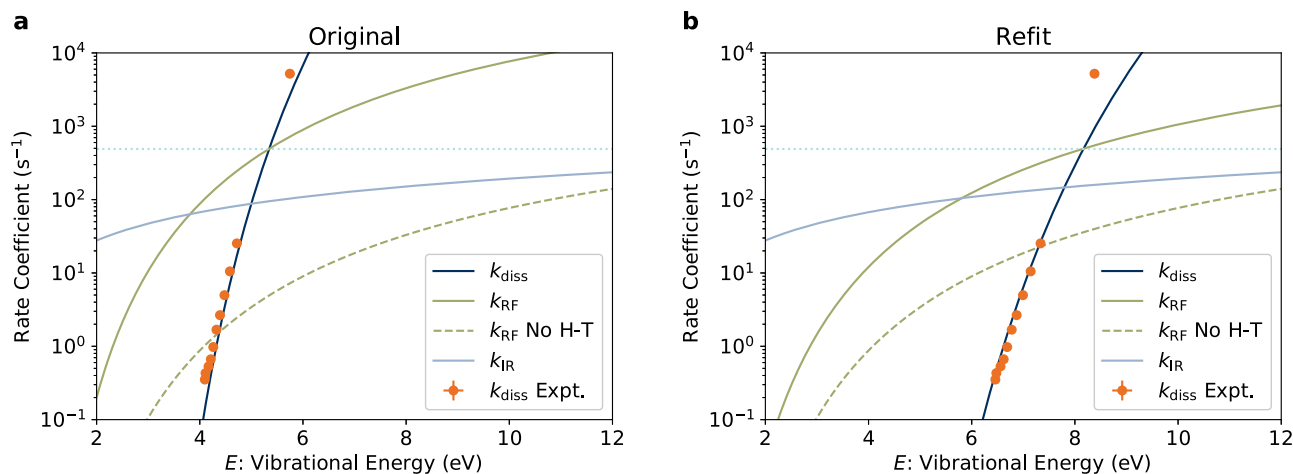
Fig. 1 | Comparison of original and refit rate coefficients. a Original rate coefficients as published in ref. 1. The dissociation rate coefficient k_{diss} is computed according to Eqn. 10 in [1] with $E_a = 3.16$ eV, and the RF rate coefficient k_{RF} is computed to Eqs. (14) and (15) in [1] using our calculated value of the oscillator strength of the $D_1 \leftarrow D_0$ transition, including Herzberg–Teller (H–T) coupling, of $f = 0.011$. **b** Refit rate coefficients with Hansen's interpretation, with $E'_a = 4.36$ eV and the oscillator strength $f' = 0.0015$ adjusted ad hoc to reproduce the

experimentally determined k_c. The horizontal dotted line in both plots passes through the crossing point between the original dissociation and RF rate coefficients and illustrates how the RF rate would need to be adjusted to achieve similar agreement with the experiment as the original rates. In both plots, the rate coefficient for RF using the calculated oscillator strength, neglecting H–T coupling, of 10^{-4} is labeled k_{RF} No H–T, and the vibrational cooling rate is k_{IR}.
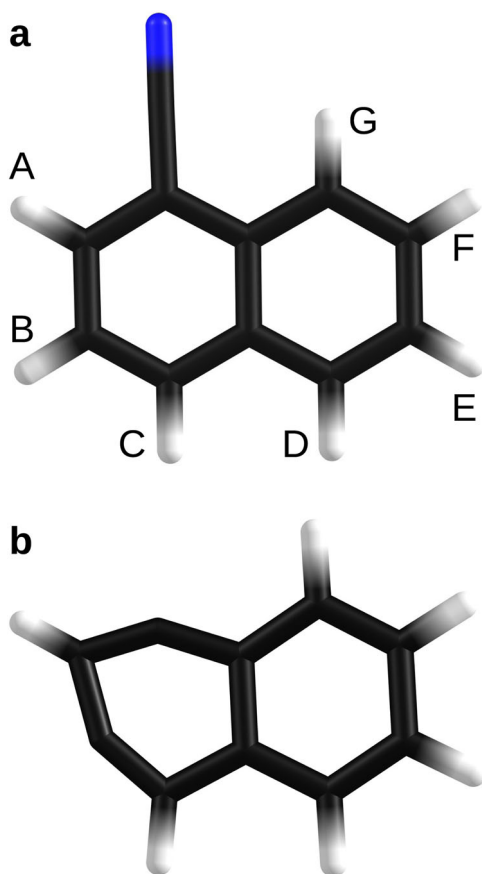
Fig. 2 | Molecular structures. a 1-CNN with H atoms labeled. **b** Lowest-energy product with H atom B removed.

Without any other adjustments to our analysis, this results in an activation energy $E'_a = 4.36(5)$ eV. Note that our value of E'_a differs from that of Hansen, who estimated the correction at a single temperature, while in our analysis, we used all data available for the range of temperatures from 1610 to 1220 K.

Figure 1 shows a comparison of the original (left) and refit (right) rate coefficients. In the right pane, the reactant energies E are given by

$$E = E_{tot}(T^{\ddagger}) + E'_a \qquad (4)$$

instead of Supplementary Eq. 6 as in our original paper, where $E_{tot}(T^{\ddagger})$ refers to the energy of the transition state. The refit value of E'_a is indeed much larger than our original value of $E_a = 3.16(4)$ eV, as well as that of "from 2.5 to 3 eV" previously reported by West et al.[7] However, it is not incompatible with our experimental results. A similar agreement between the simulated and measured rate curves, as in Fig. 2 of [1], could likely be obtained, with some modification to the RF rate coefficient. For example, a reduction of the oscillator strength of the $D_1 \leftarrow D_0$ transition to $f' = 0.0015$, from our calculated value of $f = 0.011$, would force a crossing of the dissociation and RF curves at the same critical rate coefficient (horizontal line in Fig. 1). This is still more than an order of magnitude higher than our calculated oscillator strength of 10^{-4} when Herzberg–Teller coupling is neglected[1]. So, the higher numerical value of E'_a does not change the conclusion of our paper that reproducing the measured rate requires a significant enhancement of this transition probability.

Following this re-analysis, we find the larger value of E'_a would imply that 1-CNN cations would be efficiently radiatively stabilized up to about 8 eV of internal energy, where the dissociation and RF rate coefficients are equal, rather than 5 eV with our original value of E_a. This would completely rule out the dissociation of 1-CNN$^+$ following ionization in collisions with H$^+$, the most abundant atomic cation in TMC-1, strengthening our conclusion that RF helps explain the high abundance of 1-CNN in this cloud. Since the publication of our original paper, two different groups have reported appearance energies for dissociative ionization of 1-CNN exposed to VUV radiation, which is about 7 eV above the ionization threshold[8,9], i.e., about 1 eV lower than the threshold discussed above. This discrepancy is larger than can be explained by the initial thermal energy of the neutral precursors, about 0.2 eV at 323 K sample temperature used in ref. 8. A much larger shift in the measured appearance energy in the opposite direction is rather expected as these experiments are conducted using time-of-flight mass spectrometers employing constant extraction fields. Such instruments are prone to large kinetic shifts[10]. While not completely

Table 1 | Dissociation energies for $C_{10}H_7CN^+ \longrightarrow C_{10}H_6^+ + HCN$

H atom	Diss. energy (eV)
A	4.25
B	4.18
C	4.70
D	4.44
E	4.70
F	4.72
G	4.67

The letters indicate which H atom is removed (see Fig. 2).

dispositive, the measured fragment appearance energies thus favor the lower E_a value of our original analysis.

We have calculated dissociation energies, i.e. differences in energy between reactants and infinitely separated products, for the dominant $C_{10}H_7CN^+ \longrightarrow C_{10}H_6^+ + HCN$ channel at the CCSD(T)/cc-pVTZ//ωB97X-D/cc-pVTZ level of theory as implemented in Gaussian 16.B.01[11]. The results are presented in Table 1.

The dissociation energy is a lower limit for the activation energy and, given the small observed reverse barrier, is likely a good estimate. Depending on which peripheral H atom leaves with the CN group (see Fig. 2), the dissociation energy ranges from 4.2 to 4.7 eV. This value aligns nicely with the higher value of $E_a' = 4.36(5)$ eV following Hansen's interpretation but is in tension with the above-mentioned experimental results. A detailed exploration of the dissociation potential energy surface, which is well outside the scope of this comment, should be performed to determine if lower-energy products exist, such as those resulting from isomerization of the naphthalene moiety[12,13]. Such pathways are known to be important for small PAHs[14].

The second point in the Matters Arising concerns the relationship between the measured dissociation rates $R(t)$ and the intrinsic dissociation rate coefficients $k_{diss}(E)$, and is discussed at some length in our follow-up paper[15]. This enters our analysis at Eq. 8 in [1], or Eq. 3 above in the re-analysis, which we fit to our data to determine E_a:

$$k_{diss}(E(T^\ddagger)) \approx \frac{k_B T^\ddagger}{h} e^{-E_a/k_B T^\ddagger}, \qquad (5)$$

where $T^\ddagger$ is obtained from the KER distributions. The rate coefficient $k_{diss}(E(T^\ddagger))$ is related to the measured rate $R(t)$ by Eq. 9, in which we implicitly assume:

$$R(t) = r_0 k_{diss}(E(T^\ddagger)). \qquad (6)$$

We determine the constant of proportionality r_0 empirically by a fit of the experimental data with Eq. 2 in [1]: $R(t) = r_0 t^{-1} e^{-k_c t}$. This approximation is motivated by the general principle that the most probable rate coefficient for a reaction observed at time t is $k_m = t^{-1}$. Thus, in the absence of radiation ($k_c \to 0$), the observed dissociation rate $R(t) = r_0 t^{-1} = r_0 k_m$. As explained by Hansen in his Matters Arising comment and elsewhere[16], the reactants observed to decay at time t have a narrow range of vibrational energies peaking at the energy E_m such that $k_m = k_{diss}(E_m) = R(t)/r_0$, as we assume. The effect of radiation, which reduces the vibrational energy without yielding detectable products, is to accelerate the decline in k_m by the factor $e^{-k_c t}$. The constant r_0 includes all experimental factors (see Eq. 4 in [1]) and, crucially, a dimensionless factor we call, in our follow-up paper[15], γ_0. This factor can be described as the fraction of molecules in the ensemble with vibrational energies $E \approx E_m$.

In his comment, Hansen elaborates on an expression (Eq. 3) for γ_0, which is proportional to the quantity $g(E_m)$, which is unknown but assumed by Hansen to be constant. In the analysis in [1], we instead

make the assumption explained in the previous paragraph that the most probable rate coefficient is given by $k_{diss}(E_m) t^{-1} e^{-k_c t}$, and thus that the relationship between observed rates and intrinsic rate coefficients is given by the experimentally determined constant r_0. Even if $g(E_m)$ could be directly determined from experiments without further approximations, we would not expect such a nuanced adjustment of the model parameterization to give a significantly different value of E_a.

To summarize, we have re-analyzed our data as suggested in the Matters Arising, leading to a higher activation energy for dissociation than in our original article[1]. This would not change our main conclusion, namely that hot 1-CNN cations are efficiently stabilized by fast radiative cooling, and that this could help to explain the high abundance of this molecule in space.

Data availability
The data generated in this study have been deposited in the Zenodo database. Source data are provided in this paper.

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Author contributions

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Competing interests

The authors declare no competing interests.

Additional information

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