

Isotope effects in the metastable decay of Ne_2^+

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Abstract. Neon dimer ions undergo spontaneous dissociation (metastable decay) several microseconds after formation by electron impact ionization of neon clusters. In this contribution we compare the kinetic energy release distribution (KERD) of the previously reported isotopomer $^{20}\text{Ne}_2^+$ with that of $^{22}\text{Ne}_2^+$. The heavy isotopomer shows the same two components in the KERD as the lighter ones. However, the high-energy component that is due to electronic pre-dissociation is reduced in intensity. The decrease is attributed to a reduced predissociation rate from the $\text{II}(1/2u)$ state into $\text{I}(3/2u)$.

PACS. 36.40.Qv Stability and fragmentation of clusters – 36.40.Wa Charged clusters – 33.15.Hp Barrier heights (internal rotation, inversion, rotational isomerism, conformational dynamics) – 34.30.+h Intramolecular energy transfer; intramolecular dynamics; dynamics of van der Waals molecules

1 Introduction

The most commonly encountered isotope effect in chemical dynamics arises from the mass difference; it affects the rotational constant, reduced mass and vibrational frequencies, and rates of tunneling. Other, more subtle isotope effects arise from different nuclear spins, symmetry properties, and electroweak charges of the isotopes [1, 2].

For thermally activated reactions, kinetic isotope effects are usually small, save for effects caused by the large relative mass difference between hydrogen isotopes [3]. Even if large effects exist, they will often be masked [4, 5]. For example, for unimolecular dissociations that involve a transition state with a reverse barrier, a microcanonical ensemble of small molecules with a heavy isotope may be prepared in a state just below the classical barrier (at excitation energy E^*) where the reaction can only proceed by tunneling. For the same molecule with the same energy E^* but containing a lighter isotope and correspondingly higher zero point energy of the reactant, the reac-

tion will be over the barrier, and the isotope effect will be huge. However, in a canonical ensemble the effect will be masked by the broad distribution of vibrational energies. Moreover, one also needs to consider the zero point energy in the transition state and the product states. Other effects, e.g. the kinetic shift in systems with large numbers of vibrational modes, and thermally assisted tunneling, will also complicate the situation.

The situation simplifies if one considers an ensemble of isolated dimers, excited to a long-lived electronic state that is predissociated. Even if such an ensemble does not constitute a microcanonical ensemble, each molecular ion remains frozen in its quantum state until it decays into another electronic state. A strikingly large isotope effect has been reported for N_2^+ where the rate of predissociation of the C-state in $^{15}\text{N}_2^+$ is an order of magnitude slower than in $^{14}\text{N}_2^+$, thus enhancing the rate of radiative transitions that compete with predissociation [6].

A similarly favorable situation to study kinetic isotope effects exists for neon dimer ions formed from Ne_2 by electron impact ionization. On the microsecond-time scale of the experiment, some ions will populate the $\text{II}(1/2u)$ state, see Figure 1 [7]. These ions decay via two competing pathways, either by radiative decay of the $\text{II}(1/2u)$ electronic state into the continuum of $\text{I}(1/2g)$ which immediately dissociates with an average kinetic energy release (KER) of only 6 meV, or by non-radiative decay into the strongly repulsive $\text{I}(3/2u)$ with a most probable KER of 80 meV [8, 9]. A measurement of the kinetic energy release distribution (KERD) of the products that are formed as a result of this decay thus yields the branching ratio.

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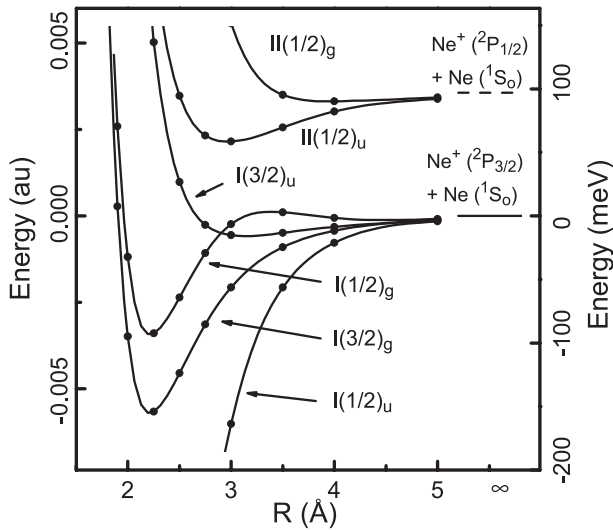


Fig. 1. Potential curves for Ne_2^+ based on ab-initio calculations [7] with spin-orbit interaction added. Curves are labeled by the projection of the total electronic angular momentum on the molecular axis, Ω , and parity (Hund's case (c)).

The transition $\text{II}(1/2u) \rightarrow \text{I}(3/2u)$ is unusual because there is no curve crossing between the initial and the final state. A similar situation also exists for HeNe^+ [10], but in heavier homonuclear rare gas dimer ions the transition does not favorably compete with the much faster radiative decay into $\text{I}(1/2g)$ [11, 12].

In our previous work we determined the KERD for spontaneous (metastable) decay of $^{20}\text{Ne}_2^+$, and successfully modeled the distributions based on ab-initio potential energy curves [7]. In the present work we compare the KERD for $^{20}\text{Ne}_2^+$ with that for $^{22}\text{Ne}_2^+$. The measurements are performed in the third field-free region of a high-resolution double focusing two sector-field mass spectrometer which offers enhanced resolution compared to measurements in the second field free region. The probability for predissociation into $\text{I}(3/2u)$ is significantly reduced in favor of the radiative decay into $\text{I}(1/2g)$.

2 Experimental

Details of the experiment have been described in previous publications [9, 13]. In short, neon dimers and clusters are produced by a supersonic expansion of neat neon gas. Neutral particles are ionized by electron impact at 120 eV. The unimolecular decomposition of mass selected dimer ions and the distribution of the kinetic energy released in the reaction (KERD) are measured by the MIKE (Mass Analyzed Ion Kinetic Energy) scan technique [5]. Reactions are analyzed in either the second (ff2) or third (ff3) field free region of the double focusing magnetic mass spectrometer that is equipped with a second electric sector [14]. Measurements in ff3 avoid possible artefacts arising from metastable reactions in ff1 that can plague measurements in ff2 [15].

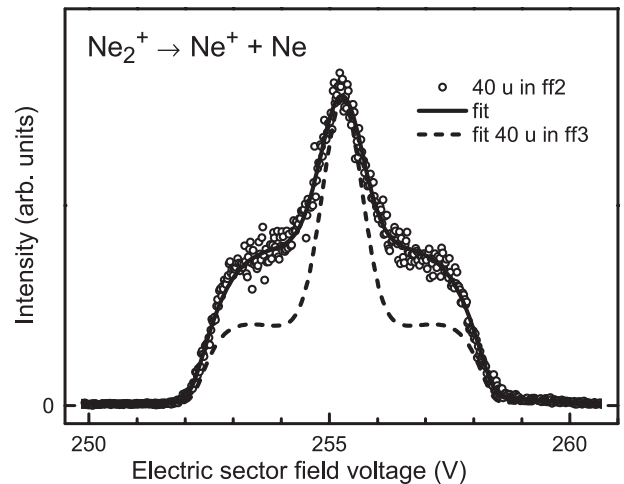
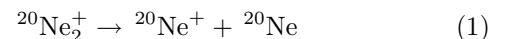


Fig. 2. MIKE spectrum recorded in ff2 for $\text{Ne}_2^+ \rightarrow \text{Ne}^+ + \text{Ne}$ for the $^{20}\text{Ne}_2^+$ isotopomer. The solid line is based on a fit but primarily used to guide the eye. The dashed line is the result of a fit to a MIKE spectrum recorded in ff3 which, because of its geometry, causes a larger discrimination against fragment ions produced with large recoil energies.

Under our conditions, the parent ion peak appears at a sector voltage of 511 V; the fragment ions of homonuclear dimer ions therefore appear at 255.5 V. Kinetic energy release distributions are derived from MIKE spectra by (i) removing statistical noise, (ii) deconvoluting the fragment ion peak with the parent ion peak, (iii) differentiating the signal with respect to the sector field voltage, and (iv) transforming the sector-field voltage scale to the kinetic energy scale. For details of the data analysis, see [16, 17].

3 Results and discussion

The upper part of Figure 2 shows a MIKE scan (open dots) for the spontaneous reaction



occurring in ff2. The striking feature of the spectrum in Figure 2 is a central peak superimposed on a much broader, roughly rectangular component. The solid line is the result of fitting a Gaussian plus a previously described expression [17] that accounts for the broad component. Variables in this expression are the width, the degree of rounding of the edges, and the degree of dish which arises from discrimination against energetic ions that are not emitted in either forward or backward direction. However, there is no theoretical basis for this particular parameterization; it is merely used to guide the eye.

The dashed line in Figure 2 shows the result of a fit to a MIKE spectrum recorded for reaction (1) in ff3; the spectrum itself will be shown further below. The spectra in Figure 2 are arbitrarily normalized at their maxima. We see that the broad component decreases in relative intensity from $\approx 48\%$ in ff2 to $\approx 26\%$ in ff3, and that it becomes dish, producing local minima in the wings of the

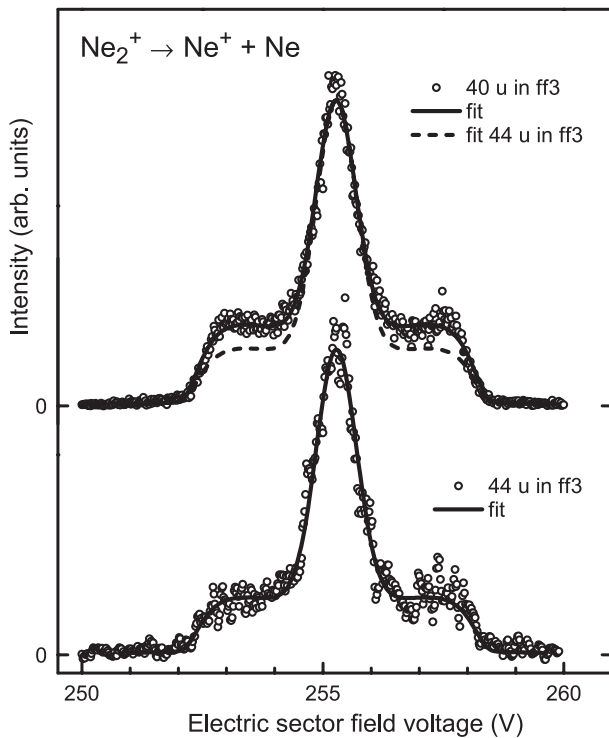
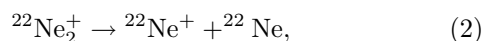


Fig. 3. MIKE spectra recorded in ff3 for $\text{Ne}_2^+ \rightarrow \text{Ne}^+ + \text{Ne}$ for two different isotopomers, $^{20}\text{Ne}_2^+$ and $^{22}\text{Ne}_2^+$ (upper and lower part, respectively). Solid lines show the result of fits. The dashed line in the upper part reproduces the fit to the $^{22}\text{Ne}_2^+$ data.

Gaussian. These two changes are correlated, i.e. stronger ion discrimination at the exit slit of E2 reduces the intensity in ff3. Although it is possible that the observed changes are solely due to discrimination, we cannot rule out that the change in time scale has some effect on the relative intensity of the broad component.

For an unbiased analysis of the data we have performed a Fast Fourier transform to reduce statistical noise, and transformed the data to a kinetic energy release distribution (KERD) [8]. The distribution is bimodal. The low-energy component which corresponds to the central peak in the MIKE spectrum rises sharply from 0, reaches a maximum at about 1 meV, and then decreases slowly. The average of this component is 6 meV. The other component of the KERD is relatively narrow and peaks around 80 meV; it corresponds to the broad and flat-topped component in the MIKE spectrum. As argued previously [8,9], the low-energy component arises from radiative decay of a bound vibronic $\text{II}(1/2u)$ state into the continuum of $\text{I}(1/2g)$; the high-energy component arises from electronic predissociation, i.e. radiationless transition from $\text{II}(1/2u)$ into a continuum $\text{I}(3/2u)$ state.

Figure 3 displays MIKE spectra (open dots) for reaction (1) and for



both recorded in ff3. The solid lines represent fits to these data. The fit to the upper spectrum was already repro-

duced in Figure 2 as a dashed line. The fit to the lower spectrum in Figure 3 is reproduced in the upper part as a dashed line.

There is a significant isotope-effect in the relative intensities of the two components. The amplitude of the broad component decreases from 26% for decay of $^{20}\text{Ne}_2^+$ to 19% for decay of $^{22}\text{Ne}_2^+$. Note that this change is not a result of ion discrimination at the exit slit because both reactions are recorded under identical geometry. Although a small difference in the relative amplitude of the two components could conceivably arise from the difference in mass and therefore the flight time of the two dimer ions, these differences (5% in time) are way too small to explain the effect (an upper limit for such a time dependence can be derived from the change of the amplitudes in Figure 2 where the time is changed drastically from ff2 to ff3). We therefore conclude that the differences in relative intensities are due to isotope effects in the spontaneous decay rates of Ne_2^+ . Within the statistical uncertainty, no isotope effect is observed in the average KER of the two contributions.

What properties of the molecular ions affect the observed KERD and, therefore, the relative intensities of the two components? Each transition from a rovibrational state of $\text{II}(1/2u)$ will give rise to a specific KER; it has to be weighted with the probability that the initial state is populated when the ion enters the field-free region, times the probability that the state decays into another electronic state which immediately, within $\ll 1 \mu\text{s}$, dissociates into $\text{Ne}^+ + \text{Ne}$. We make the reasonable approximation that the population of each rovibrational $\text{II}(1/2u)$ state decays exponentially; i.e. we discard the possibility of transitions within the $\text{II}(1/2u)$ manifold, and the possibility that $\text{II}(1/2u)$ may be populated at $t > 0$ by transitions from higher electronic states. Then the weight factors are

$$P_{vJ}(t_{\text{exp}}) = p_{vJ}(0)k_{vJ} \exp(-k_{vJ}t_{\text{exp}}) \quad (3)$$

where $t = 0$ corresponds to the instant of ionization by electron impact, and t_{exp} is the geometric average of the experimental time window $[t_1, t_2]$ which is assumed to be narrow, $\Delta t \ll t_{\text{exp}}$ ($t_{\text{exp}} = 12.0$ and $19.5 \mu\text{s}$ for decay of $^{20}\text{Ne}_2^+$ in ff2 and ff3, respectively). The initial populations $P_{vJ}(0)$ depend on the population of rovibrational states of Ne_2 in the cluster beam and the Franck-Condon factors for transitions to $\text{II}(1/2u)$ upon electron impact.

There are several factors that will affect the relative intensities of the two components in the KERD: (i) the population of rovibrational states of Ne_2 in the cluster beam (arising from different energies plus, perhaps, different temperatures for different isotopomers), and (ii) the initial population $P_{vJ}(0)$ of the rovibrational $\text{II}(1/2u)$ states, their energies and their lifetimes (decay rates) with respect to radiative decay into $\text{I}(1/2g)$ or non-radiative transition into $\text{I}(3/2u)$.

We have discussed the theoretical modeling in detail in our previous work on $^{20}\text{Ne}_2^+$ [9]. We obtained good agreement between experiment and theory for the overall shape of the two components of the KERD, but the relative intensity of the broad component was overestimated.

The limited accuracy of the theoretical potential energy curves [7] may have caused the discrepancy. Another, probably more important factor is the use of the golden rule which generally accounts for transition energies in quantitative detail, but not for rates. The latter often deviate from their experimental values by factors of two to three [18]. A third factor may be an incorrect estimate of the temperature of the neutral dimer in the cluster beam for which we assumed 10 K, estimated from a measurement of the dimer temperature of Ar₂ by Raman scattering [19] and established thermodynamic scaling rules for atomic clusters [20].

In view of these uncertainties we have not attempted to calculate the isotope dependence of the KERD and, in particular, the relative intensities of the two components. However, we conjecture that the main isotope effect enters through the predissociation rate for $\Pi(1/2u) \rightarrow I(3/2u)$. A larger mass will correspond to a more localized wave packet for the initial state of Ne₂⁺ and, thus, to a reduced rate. The expression in equation (3) reaches a maximum if $k = 1/t_{\text{exp}}$. Hence, a reduced rate may either increase or decrease the weight of the broad component. However, for decay of ²⁰Ne₂⁺ we computed a rate $k = 5 \times 10^3 \text{ s}^{-1}$ [9] which is a factor of 10 smaller than $1/t_{\text{exp}}$, hence a decrease in the rate will imply a smaller weight factor.

Another interesting kinetic isotope effect could arise from a change in symmetry. Our experiments involve symmetric (homogeneous) dimers. As demonstrated by Pack and Walker [2], the reduced symmetry of mixed isotopomers will impact rates of dissociation as well as recombination reactions. It would be interesting to search for this effect in ²⁰Ne²²Ne⁺.

In conclusion, we have recorded MIKE spectra for spontaneous decay of ²⁰Ne₂⁺ and ²²Ne₂⁺. The two components that contribute to these MIKE spectra are similar in shape for the two isotopomers, but they differ in relative intensity. The heavier isotopomer is characterized by a weaker high-energy component which we assign to a reduced rate for radiationless decay from $\Pi(1/2u)$ into $I(3/2u)$. This transition is unusual because the two potential energy curves do not intersect. It would be interesting to measure MIKE spectra for the isotopically mixed ²⁰Ne²²Ne⁺ to identify the effect of reduced symmetry on the kinetics.

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