

**Non-sticking of helium buffer gas to hydrocarbons**

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Lifetimes of complexes formed during helium-hydrocarbon collisions at low temperature are estimated for symmetric-top hydrocarbons. The lifetimes are obtained using a density-of-states approach. In general the lifetimes are less than 10–100 ns and are found to decrease with increasing hydrocarbon size. This suggests that clustering will not limit precision spectroscopy in helium-buffer-gas experiments. Lifetimes are computed for noble-gas benzene collisions and are found to be in reasonable agreement with lifetimes obtained from classical trajectories as reported by J. Cui *et al.* [*J. Chem. Phys.* **141**, 164315 (2014)].

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**I. INTRODUCTION**

In the gas phase, no two molecules can truly stick upon colliding, unless some mechanism for releasing their binding energy exists. Most often, this mechanism involves a third molecule; hence molecule clustering proceeds more slowly as the density of the gas is reduced. Thus in molecular-beam expansions, the occurrence of seed-gas atoms (typically noble gasses) adhering to entrained molecular species can be controlled by varying the pressure of the expansion. Likewise, reduced three-body recombination rates in extremely rarefied ultracold gases are what allow phenomena such as Bose-Einstein condensation to be studied at all.

More precisely, three-body recombination, scaling as  $n^3$  (where  $n$  is the number density), dwindles for small  $n$  in comparison to the two-body collision rate, which scales as  $n^2$ . A complication occurs when the two-body collisions result in the formation of a collision complex with a sufficiently long lifetime  $\tau$  that collision with another molecule can occur during the interval  $\tau$ , resulting in a bound state of two particles and a release of energy, a process known as the Lindemann mechanism (Ref. [1], pp. 215–219). The importance of this mechanism relies crucially on the scale of  $\tau$  for a given low-density gas. Recently, it has been suggested, although not yet empirically verified, that  $\tau$  can grow quite long for extremely low temperature gases, even of the order of 100 ms for alkali-metal dimer molecules colliding in microkelvin gases [2]. If true, this process would lead to the decay of such a gas.

Between the regimes of supersonic jet expansions and ultracold molecules lies a host of experiments on cold molecules, notably, those cooled to the temperature of an ambient helium buffer gas in a cold cell at temperatures on the order of 1–10 K. The buffer-gas cell has proven to be a reliable source of cold molecules, at temperatures sufficiently low to extend the reach of precision spectroscopy [3–6]. The success of these experiments requires the helium buffer gas not to stick to the molecules under study, as the spectral lines would thereby be shifted. Under typical experimental conditions, the collision rate of the buffer gas with the molecule is tens of microseconds [7]; spectroscopy is safe if the collision complex lives for shorter times than this.

Thus far, no empirical evidence has emerged suggesting that the sticking occurs in the buffer-gas environment [3,7–10], a conclusion that is supported by detailed classical trajectory calculations [11–13]. This appears to be true even

for a relatively floppy molecule such as trans-stilbene, for which comparatively low energy vibrational modes might have been expected to promote sticking [7]. The existing evidence suggests, therefore, that the transient lifetime of a hydrocarbon-helium complex in the buffer-gas cell remains comfortably less than about a microsecond.

In this article we argue that such short lifetimes are natural and perhaps even generic under these circumstances. The argument is based on considerations drawn from the theory of unimolecular dissociation, in which a complex molecule with sufficient energy to dissociate nevertheless experiences a time delay before actually doing so. In this theory, the dwell time of the complex stands at the balance between excitation of degrees of freedom that cannot dissociate while conserving energy (thus contributing to longer dwell times) and degrees of freedom that can (thus contributing to shorter dwell times). For complexes consisting of a hydrocarbon molecule with a transiently attached helium atom, both these densities of states may increase with increasing molecule size, so that the dwell time  $\tau$  depends weakly on the specific hydrocarbon. Based on simple ideas, we give order-of-magnitude estimates for typical lifetimes in such a gas.

**II. BUFFER-GAS ENVIRONMENT**

We contemplate a buffer-gas cell, in thermal equilibrium at temperature  $T$ , containing helium gas with number density  $n_a$  and hydrocarbon molecules with density  $n_m \ll n_a$ , in which case the majority of collisions the molecules suffer will be with atoms. Upon introducing molecules into the gas, atom-molecule collisions occur at a rate  $K_{am}n_a n_m$ , defined by a rate constant  $K_{am}$ . In the Lindemann model, these collisions produce short-lived collision complexes that are characterized by number density  $n_c$  and that decay at a mean rate  $\gamma = 1/\tau$ . Under these circumstances the atomic density is not significantly depleted, and the collisions are described by the rate equations

$$\begin{aligned}\dot{n}_m &= -K_{am}n_a n_m + \gamma n_c, \\ \dot{n}_c &= K_{am}n_a n_m - \gamma n_c.\end{aligned}\quad (1)$$

After an equilibration time  $\sim (K_{am}n_a)^{-1}$ , the fraction of molecules temporarily absorbed in complexes is

$$\frac{n_c^{eq}}{n_m} \approx K_{am}n_a\tau, \quad (2)$$

a fraction that is negligible unless the dwell time  $\tau$  is at least comparable to the inverse collision rate.

To place approximate numbers to this constraint, consider a typical helium number density of  $n_a = 2 \times 10^{14} \text{ cm}^{-3}$  [7] and a collision cross section approximated by the Langevin capture cross section (Ref. [1], pp. 91–93),

$$\sigma_L = \pi \left( \frac{3}{2} \right)^{2/3} \left( \frac{6C_6}{2k_B T} \right)^{1/3} \approx 3 \times 10^{-14} \text{ cm}^2, \quad (3)$$

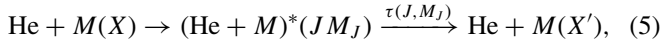
assuming a van der Waals coefficient of  $C_6 = 100$  atomic units (see below). The atom-molecule rate constant is then  $K_{am} = \bar{v}\sigma_L \approx 6 \times 10^{-10} \text{ cm}^3/\text{s}$ , whereby the fraction of complexes is approximately

$$\frac{n_c^{eq}}{n_m^{eq}} \approx \frac{\tau}{10 \mu\text{s}}. \quad (4)$$

Thus for dwell times significantly less than  $10 \mu\text{s}$ , the complexes should be rare. In what follows, we estimate the lifetime, finding it to be at most 10–100 ns. Therefore in the buffer gas we expect fewer (probably far fewer) than one molecule in a hundred to be involved in a collision complex at any given time.

### III. RATES AND LIFETIMES

We are interested here in identifying an upper bound for the sticking lifetime of helium atoms on hydrocarbon molecules. The sticking process is denoted schematically as



where  $X$  are a set of quantum numbers, including molecular rotation  $N$ , which completely describe the state of the molecule. For the duration of the collision, the atom and molecule are assumed to reside in a complex with total angular momentum  $J$ . This angular momentum is regarded as the vector sum, in the quantum-mechanical sense, of the molecule's rotation  $N$  and the partial wave of the atom-molecule relative motion  $L$ .  $\tau(J, M_J)$  is the lifetime of a complex for total angular momentum  $J$  and projection  $M_J$ .

At a given collision energy  $E_c$ , collisions can occur in any of a set of incident channels, whose number is the number of energetically open channels  $N_0(J, M_J)$  for a given total angular momentum. The relevant mean sticking lifetime in the experiment is therefore the lifetime of each collision complex averaged over all  $J$  and  $M_J$  combinations and weighted by the number of incident channels leading to that combination:

$$\bar{\tau} = \frac{\sum_{J, M_J} \tau(J, M_J) N_0(J, M_J)}{\sum_{J, M_J} N_0(J, M_J)}. \quad (6)$$

Within the Rice-Ramsperger-Kassel-Marcus (RRKM) model [1, 14, 15] the dwell time of a complex is approximated as

$$\tau(J, M_J) = 2\pi \hbar \frac{\rho(J, M_J)}{N_0(J, M_J)}, \quad (7)$$

where  $\rho(J, M_J)$  is the density of available rovibrational states [density of states (DOS)] of the complex for the given total an-

gular momentum. Thus the mean sticking lifetime is given by

$$\bar{\tau} = 2\pi \hbar \frac{\sum_{J, M_J} \rho(J, M_J)}{\sum_{J, M_J} N_0(J, M_J)}. \quad (8)$$

It must be emphasized that this approximation is an upper limit to the lifetime, as it assumes that all the possible states contributing to  $\rho$  are, in fact, able to be populated in a collision. This assumption disregards, for example, barriers in the potential-energy surface that forbid a given entrance channel from probing a certain region of phase space. This circumstance would reduce the effective density of states and hence also the lifetime.

### IV. DENSITY OF STATES

Following Mayle *et al.* [2, 16] we estimate the density of states  $\rho(J, M_J)$  using a counting procedure. This procedure begins by somewhat artificially separating the degrees of freedom of the He-molecule complex into those coordinates  $\{\mathbf{X}\}$  necessary to describe internal motions of the molecule and a coordinate  $\mathbf{R}$  giving the relative motion of the atom and molecule. The enumeration of molecular states follows from the spectrum of the molecule. The atom-molecule states are approximated by postulating a schematic atom-molecule potential  $V(R)$ .

For a given molecular state with energy  $E(X)$ , the potential  $V_{X,L}(R) = V(R) + \hbar^2 L(L+1)/2\mu R^2 + E(X)$  is constructed, so long as  $L$  and the molecular rotation are consistent with the total angular momentum  $J$  under consideration. The number of bound states  $N_{am}(X, L)$  of  $V_{X,L}$ , lying within an energy range  $\Delta E$ , centered around the collision energy, is found. The density of these states is then given by the sum

$$\rho(J, M_J) = \frac{1}{\Delta E} \sum'_{X,L} N_{am}(X, L). \quad (9)$$

The prime on the summation sign is a reminder that the sum is taken over those quantum numbers for which energy and angular momentum conservation are satisfied.

In the model, the potential  $V(R)$  is assumed to be of Lennard-Jones form. This potential has a realistic van der Waals coefficient for the He-hydrocarbon interaction, as well as a reasonable minimum. A key point in the lifetime analysis is that the parameters of this potential are *weakly dependent* on the particular hydrocarbon involved. Table I shows the equilibrium distance, van der Waals coefficient, and energy minimum for a variety of helium-hydrocarbon systems. While Table I comprises a variety of hydrocarbons of different shapes and sizes, the equilibrium distance and energy minimum vary little between them. This is because the helium atom interacts with only the nearby atoms in the hydrocarbon. Further, the reduced mass for the collision of a hydrocarbon with helium is, to a very good approximation, simply the helium mass.

Thus the potentials  $V_{X,L}(R)$  and the numbers of states  $N_{am}(X, L)$  that they hold vary little between different helium-hydrocarbon systems. We therefore make the approximation

$$\rho(J, M_J) \leq \rho_{am} \sum'_{X,L} 1 \equiv \rho_{am} N_m(J, M_J), \quad (10)$$

TABLE I. Equilibrium distance and energy minimum for the helium-hydrocarbon interaction for a variety of different systems. Equilibrium distance and potential were obtained in GROMACS [17] with the OPLS-AA force field [18,19]. In each case, these data can be used to construct a schematic Lennard-Jones potential  $V(R)$ , leading to the atom-molecule density of states factor  $\rho_{am}$ , defined in (11).

System	$R_e$ (Å)	$V^{\min}$ (K)	$C_6$ (a.u.)	$\rho_{am}$ (K $^{-1}$ )
Helium+methane	3.2	52	16	0.05
Helium+ethane	3.3	77	27	0.03
Helium+propane	3.7	82	62	0.03
Helium+butane	3.5	108	59	0.02
Helium+pentane	3.2	126	41	0.02
Helium+hexane	3.4	131	55	0.02
Helium+benzene	3.0	130	30	0.02
Helium+naphthalene	3.2	159	45	0.01
Helium+propandiol	3.4	115	56	0.02

where  $N_m(J, M_J)$  is the number of states of the molecule consistent with angular momentum and energy conservation. The quantity  $\rho_{am}$  is a kind of representative atom-molecule density of states. It is conveniently approximated by the inverse of the lowest vibrational excitation,

$$\rho_{am} = \frac{1}{E_{v=1, L=0} - E_{v=0, L=0}}. \quad (11)$$

Thus the complex lifetime is approximately bounded above by

$$\bar{\tau} \approx 2\pi\hbar\rho_{am} \frac{\sum_{J, M_J} N_m(J, M_J)}{\sum_{J, M_J} N_o(J, M_J)}. \quad (12)$$

Here the first factor has a generic approximate value for any He-hydrocarbon interaction, of the order of  $10^{-12}$  s, while the second factor elaborates on the distinction between different molecules. Upon increasing the density of states of the molecule, both the numerator and the denominator of this factor could increase. The counting exercise must be done to find its ultimate effect on the molecular lifetime.

## V. EFFECT OF ROTATIONAL STATES

Rotational splittings in large hydrocarbons tend to be small compared to the collision energy in a buffer gas  $\Delta E_{\text{rot}} \ll E_c \approx 10$  K, while in general the vibrational splitting is larger  $\Delta E_{\text{vib}} > E_c$ . The dominant contribution to  $N_m$  and  $N_o$  in Eq. (12) arises therefore from the rotational levels of the molecule. Figure 1 shows the lowest rotational energy levels for both hexane and benzene. The rotational constants were obtained from the Computational Chemistry Comparison and Benchmark Database (CCCBDB) [20], and the energy levels were computed with PGOPHER [21]. It is seen that these two systems have rather different rotational energy levels.

Specifically, these molecules are, to a good approximation, characterized as symmetric-top molecules, that is, rigid rotors with cylindrical symmetry. Such rotors are characterized by two rotational constants  $A$  and  $B$  for rotation around and orthogonal to the symmetry axis, respectively, and yield a spectrum

$$E(N, K) = BN(N+1) + (A-B)K^2, \quad (13)$$

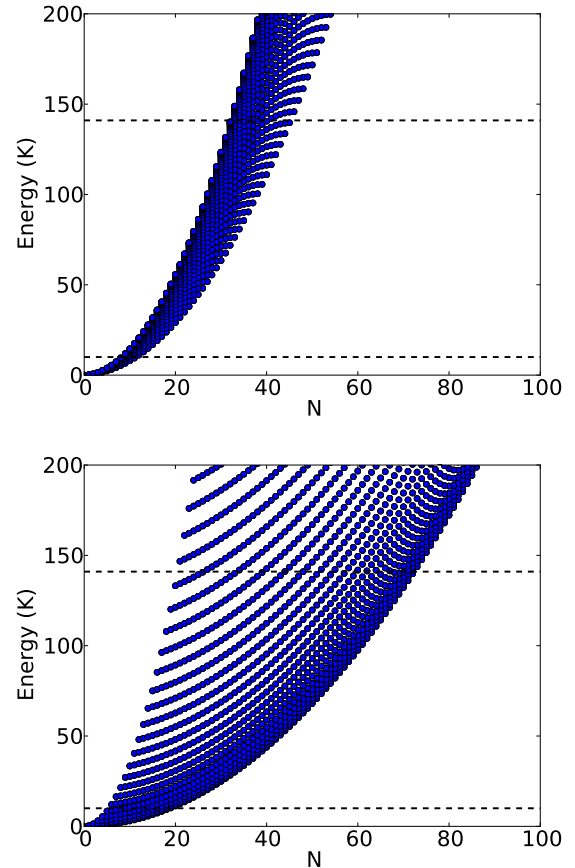


FIG. 1. (Color online) Rotational energy levels for (top) hexane and (bottom) benzene. The dashed lines show the collision energy  $E_c = 10$  K and the highest possible threshold energy that can contribute to the DOS,  $|V_{L=0}(R_{\min})| + E_c$ . While hexane has more levels above  $E_c$  that can contribute to sticking, it also possesses more levels below  $E_c$  that can lead to dissociation of the atom-molecules complex.

where  $N$  is the total angular momentum quantum number and  $K$  is the projection of  $N$  along the axis of symmetry of the rotor. Note that when  $A = B$ , the rotor is spherically symmetric and the familiar rotational spectrum  $BN(N+1)$  is obtained.

Hexane ( $C_6H_{14}$ ) is a linear-chain molecule; hence its symmetric-top analog is a prolate rigid rotor with  $A > B$ . Its spectrum is shown in the top panel of Fig. 1. For each value of  $N$ , the spectrum starts at an energy  $BN(N+1)$  and adds to it additional energies  $(A-B)K^2$  for values of  $K$  from  $-N$  to  $N$ . In contrast, benzene ( $C_6H_6$ ) is a ring molecule whose symmetric-top analog is oblate, with  $A < B$ . In this case, for a given  $N$ , a series of levels is generated that is lower than the basic energy  $BN(N+1)$ . For this reason, benzene has comparatively more “low-energy” rotational excitations and could be expected to possess a slightly higher density of states and hence a slightly longer sticking lifetime.

To orient these rotational spectra in terms of the sticking model, Fig. 1 shows two dashed lines. The lower line is 10 K, the approximate collision energy at buffer-gas temperatures. The upper line represents the collision energy plus the depth of the schematic potential  $V(R)$  between the atom and the molecule, a quantity denoted  $E_{\text{max}} = E_c + |V_{L=0}(R_{\min})|$ .

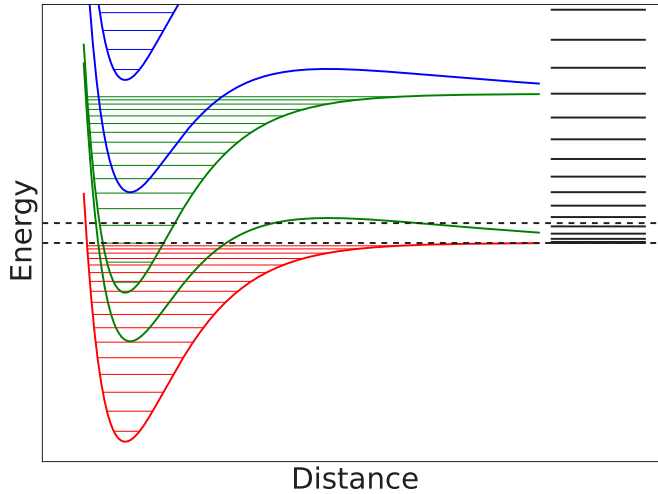


FIG. 2. (Color online) Schematic showing contributions to  $N_m$  and  $N_o$ . The dashed horizontal lines represent zero energy and the collision energy. The horizontal solid black lines on the right represent rotational levels of the molecule  $E(N)$ . Combinations of  $N$  and  $L$  consistent with angular momentum conservation lead to potentials  $V_{N,L}$ , only a few of which are shown for clarity. Potentials  $V_{N,L}$  whose minimum lies below the collision energy contribute to  $N_m$ ; these potentials are colored green (light gray). Likewise, potentials  $V_{N,L}$  with a threshold and centrifugal barrier below the collision energy contribute to  $N_o$  and are colored red (medium gray). Potentials which cannot contribute to either are colored blue (dark gray).

Ignoring for the moment considerations of angular momentum conservation, the total number of states belonging to any potential  $V_{X,L}$  and lying in energy below  $E_{\max}$  denotes potentially resonant states that contribute to increasing the lifetime; states higher in energy than this do not satisfy energy conservation.

In more detail, the number of states  $N_m$  must be counted in a way consistent with the conservation of angular momentum. Thus for a given fixed total  $J$  the possible rotation  $N$  and partial wave  $L$  quantum numbers are considered, and the potential  $V_{N,L} = V(R) + \hbar^2 L(L+1)/2\mu R^2 + E(N)$  is constructed. If the minimum of this potential lies below the collision energy, then this state is energetically allowed and is counted as part of  $N_m$ ; otherwise, it is not (see Fig. 2). Likewise, if the centrifugal barrier of the potential  $V_{N,L}$  lies below the collision energy, then the state is counted toward the number of open channels  $N_o$ . Otherwise, the collision is assumed not to tunnel through this barrier and does not count as an entrance or exit channel. This requirement is essentially the same as that assumed in the Langevin capture model of collisions.

Computing the sum in this way, we find lifetimes of hexane and benzene to be approximately 36 and 44 ps, respectively. Gratifyingly, the lifetime for benzene is consistent with the far more detailed classical trajectory calculations of Cui *et al.* [11].

Within this counting model, we can consider the lifetimes for many hypothetical molecules, characterizing their rotational spectra by the symmetric-top energy levels (13), for various values of the rotational constant  $A$  and  $B$ . These lifetimes assume, as above, that  $\rho_{am}$  is approximately the same for all such molecules. To make the calculation concrete, we

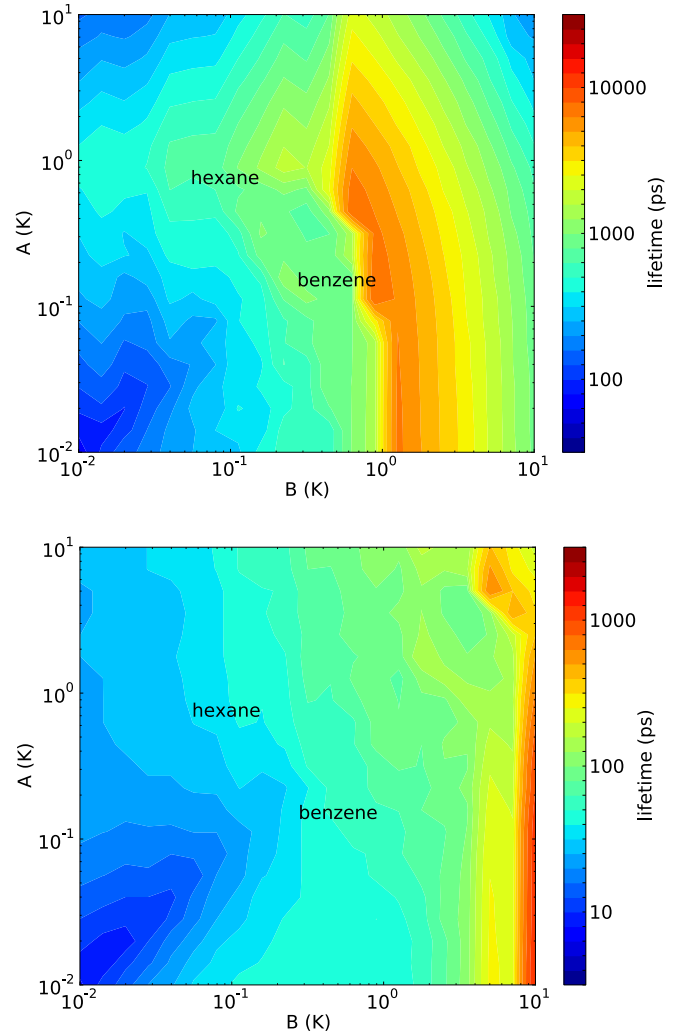


FIG. 3. (Color online) Lifetime of helium symmetric-top molecule clusters as a function of rotational constants  $A$  and  $B$  at (top)  $E_c = 1$  K and (bottom)  $E_c = 10$  K, using  $\rho_{am}$  and  $V_{L,N}$  as for hexane. Labeled are the lifetimes for the prolate-top hexane and oblate-top benzene; the point labeled is at the bottom left of the word.

assume the same values of  $\rho_{am}$  and the schematic potentials  $V_{L,N}$  as for hexane.

Figure 3 shows the lifetime of symmetric-top molecules within this model as a function of rotational constants  $A$  and  $B$  at two different collision energies,  $E_c = 1$  and 10 K. The longest lifetimes for both collision energies occur when  $B \approx E_c$ . The lifetime is only weakly dependent on  $A$ . As  $B$  decreases below  $E_c$ , the lifetime rapidly decreases because in this circumstance rotational levels lying below  $E_c$  contribute to  $N_o$  in addition to  $N_m$ . In addition, as  $B$  increases above  $E_c$ , the lifetime slowly decreases as rotational levels are pushed higher, and fewer of them contribute to  $N_o$ . We therefore conclude that maximum lifetimes occur when  $B \gtrsim E_c$ . Finally, for a given molecular spectrum, the lifetimes are larger for lower collision energy  $E_c$  since relatively more of the molecular states contribute to  $N_m$  than to  $N_o$ .

For buffer-gas experiments at 10 K this means the maximum lifetime actually occurs for light species such as methane,



where  $B = 7.6$  K. This lifetime is around 1 ns, well below the 10  $\mu$ s required for clustering to occur. This result is quite promising for the prospect of cooling large hydrocarbons. It is also worth remembering that the RRKM lifetime is an upper bound on the actual lifetime as it assumes ergodicity, an assumption that appears to be justified for helium-benzene collisions [11].

These remarks are derived for symmetric-top molecules, but little should change for asymmetric-top molecules. The lifetime of a symmetric rotor at a given buffer-gas temperature is primarily determined by its principal rotational constant  $B$ . The rotational energy levels of an asymmetric top are intermediate between prolate and oblate limits. As such it is expected that, as with symmetric tops, the lifetime of asymmetric tops will also be primarily determined by  $B$ .

Thus far we have considered lifetimes of collision complexes of helium with large hydrocarbons, but one may also contemplate a buffer gas cooling large biological molecules such as Nile red [7]. In general such molecules have a hydrocarbon backbone with functional groups containing elements such as oxygen, nitrogen, etc. While the interaction of helium with such elements can be stronger (compare propandiol and propane in Table I), this should be a minor effect. Indeed, our model suggests that the estimated lifetimes for propane and propandiol are 54 and 39 ps, respectively.

## VI. INFLUENCE OF VIBRATIONAL STATES

Including vibrational energy levels of the molecule will presumably increase the lifetime of the complex by increasing the density of states  $\rho$  without significantly increasing the number of open channels  $N_o$  (this latter fact follows because the vibrational constant is likely to be larger than 10 K). The longest increase in lifetime will occur when a vibrational level exists just above the collision energy  $\Delta E_{\text{vib}} \gtrsim E_c \approx 10$  K, so that it contributes to  $N_m$  but not to  $N_o$ . Even in this case, perhaps ten vibrational levels would occur in the energy range up to  $E_{\text{max}}$ , meaning that the lifetimes could increase from the estimates in the previous section by perhaps an order of magnitude, up to tens to hundreds of nanoseconds at  $E_c = 10$  K. This short lifetime is consistent with the lack of clustering observed in trans-stilbene and Nile red, for which low-energy vibrational modes might have been expected to promote sticking [7].

## VII. ALTERNATIVE NOBLE GASES

Other noble-gas (NG) atoms are potential candidates for buffer-gas cooling and supersonic-expansion experiments [22]. Cui *et al.* [11] have reported noble-gas benzene complex lifetimes for temperatures in the range 5–10 K from classical-trajectory simulations. Table II compares the DOS lifetimes with those of Cui *et al.* at 10 K. We compute lifetimes separately for each of the cross sections of the NG-benzene potential reported in [11]. As for the classical trajectory lifetimes, the DOS lifetime increases with NG mass, as deeper potentials lead to higher  $N$  and  $L$  quantum numbers contributing to  $N_m$ .

The DOS lifetimes always overestimate the classical-trajectory lifetime by an amount that increases with the mass

TABLE II. Lifetimes for noble-gas benzene complexes for both DOS lifetimes using cross sections of the NG-benzene potential and classical-trajectory lifetimes reported in [11].

System	$\tau$ (ps)			Cui <i>et al.</i>
	Out of plane	Vertex in plane	Side in plane	
Helium	40	40	30	$\sim 10$
Neon	260	240	140	$\sim 50$
Argon	1380	1080	640	$\sim 100$
Krypton	2900	1990	1230	$\sim 150$
Xenon	4470	2990	1920	$\sim 200$

of the NG atom. The DOS lifetime assumes ergodicity; that is, the full density of rotational states is actually populated in a collision. If this is not the case, then the lifetime of the cluster is reduced. We interpret the increasing overestimation of the lifetime, with NG mass, as a hint that high rotational states available in the collision are not necessarily populated. For example, the NG gas atom may be confined to only one side of the benzene molecule. Nevertheless, the estimates for experimentally relevant helium buffer gas remain fairly accurate in cases where the comparison can be made.

## VIII. CONCLUSIONS

In the present work we have developed a method for estimating helium-hydrocarbon complex lifetimes using a density-of-states approach at low collision energies. This model distinguishes between degrees of freedom that do not have energy to dissociate (contributing to longer lifetimes) and degrees of freedom that do (contributing to shorter lifetimes). The lifetime of a complex is determined by the balance between them. We obtain lifetimes for generic symmetric-top hydrocarbons, finding that the lifetime decreases with increasing hydrocarbon size. This result is extremely encouraging for using helium as a buffer gas for cooling large biological molecules, which relies on helium buffer gas not sticking to the molecules. This result is in agreement with all empirical evidence [3,7–10] and other theoretical calculations [11–13] based on classical trajectories. Our approach complements these calculations, enabling a rough survey of molecular species and their behavior in the buffer-gas environment.

Finally, we note that in some case the lifetimes are not always many orders of magnitude below 10  $\mu$ s, and in some cases they may be as high as tens to hundreds of nanoseconds. Moreover, lifetimes increase at lower collision energies, while collision rates increase at higher buffer-gas densities. Thus sticking may be an observable effect in slightly colder, denser helium cells for well-chosen molecules.

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