

POTENTIAL ENERGY CURVE OF N<sub>2</sub> REVISITEDVladimír ŠPIRKO<sup>a,\*</sup>, Xiangzhu Li<sup>b1</sup> and Josef PALDUS<sup>b2</sup><sup>a</sup> Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, v.v.i., Center for Biomolecules and Complex Molecular Systems,

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*Dedicated to Dr. Zdeněk Havlas on the occasion of his 60th birthday.*

Recently generated ground state potential energy curves (PECs) for the nitrogen molecule, as obtained with the reduced multireference (RMR) coupled-cluster (CC) method with singles and doubles (RMR-CCSD), and its version corrected for the secondary triples RMR-CCSD(T), using cc-pVXZ basis sets with X = D, T, and Q, as well as the extrapolated complete basis set (cbs) limit (X. Li and J. Paldus: *J. Chem. Phys.* **2008**, *129*, 054104), are compared with both the highly accurate theoretical configuration interaction PEC of Gdanitz (*Chem. Phys. Lett.* **1998**, *283*, 253) and analytic PECs obtained by fitting an extensive set of experimental data (R. J. Le Roy et al.: *J. Chem. Phys.* **2006**, *125*, 164310). These results are analyzed using a morphing procedure based on the reduced potential curve (RPC) method of Jenč. It is found that an RPC fit of both theoretical potentials can be achieved with only a few parameters. The RMR PECs are found to provide an excellent description of experimentally available vibrational levels, but significantly deviate from those of Gdanitz's PEC for highly stretched geometries, yet still do provide a qualitatively correct PECs that lie within the region delimited by Le Roy's analytical PECs.

**Keywords:** Reduced multireference coupled-cluster method; Reduced potential curve method; Nitrogen molecule potential energy curves.

A quantitatively correct description of highly-excited ro-vibrational states of molecular systems that is based on the Schrödinger equation for the nuclear motion requires a knowledge of accurate potential energy functions defined over a wide range of vibrational displacements. Although such a task is simple in principle, the actual determination of relevant potential functions represents a rather challenging problem, both for experiment and theory. A straightforward RKR inversion or fitting of experimental data is

greatly limited by a notorious scarcity of required experimental data and theoretically evaluated potential functions do not always possess a requisite accuracy for spectroscopic applications.

A particularly difficult problem in a theoretical generation of potentials arises when dealing with instances or states possessing a multireference character, which require a proper treatment of electron correlation effects due to the presence of quasidegeneracy. Although these problems may arise already at the equilibrium geometry – as in the case of the beryllium dimer where we encounter quasidegeneracy already in the atomic orbitals of the unbound Be atoms (see, e.g., ref.<sup>1</sup>) – they invariably arise when dissociating genuine chemical bonds into open-shell fragments or, in fact, for general open-shell species as represented by various multiradicals (see, e.g., ref.<sup>2</sup>; for a general account see, e.g., refs<sup>3–6</sup>). The problem becomes particularly severe when breaking multiple bonds, as is the case for the nitrogen molecule.

All the above mentioned cases call for multireference (MR) type approaches, be they of the variational configuration interaction (CI) or perturbative coupled-cluster (CC) variety. The MR CI approaches are conceptually simple (see, e.g., refs<sup>7,8</sup>), but their convergence is generally very slow, requiring an explicit consideration of a very large number of configuration state functions. Moreover, while these approaches, with a proper choice of reference configurations, can efficiently account for nondynamic correlations, they are not size-extensive. For this reason, a plethora of empirical Davidson-type corrections has been developed, particularly in the MR case (see, e.g., refs<sup>8–13</sup>). On the other hand, the CI approaches can be easily symmetry adapted and supply simultaneously an information about the excited states. In contrast, the standard CC approaches are size-extensive by their very nature (see, e.g., refs<sup>6,14,15</sup>, and references therein). Yet, their most common single reference (SR) version with singles (S) and doubles (D), the SR-CCSD method<sup>6,14,15</sup>, cannot handle static and nondynamic correlations or quasidegeneracy, while their MR varieties are generally more complex and their implementation is often plagued by various shortcomings (intruder states, complete model space requirement, etc.). For this reason the emphasis has been lately on the so-called state selective or state specific (SS) approaches that exploit MR CC formalism, in one way or another, but focus on one state at a time (for a brief overview, see, e.g., refs<sup>16,17</sup>). Both CI and CC approaches have been employed to generate highly-accurate potential energy curves (PECs) for the nitrogen molecule. In the CI case, the benchmark results were generated by Gdanitz<sup>18</sup> by relying on the explicitly correlated ( $r_{12}$ )-MR-CI(SD) or ( $r_{12}$ )-MR-ACPF method. In the CC case, rather accurate PEC's for nitrogen were recently generated<sup>19</sup>

by relying on the so-called reduced MR (RMR) CCSD approach<sup>20–22</sup>. This method is of the externally-corrected (ec) variety<sup>4,14,23</sup> and exploits an important subset of (primary) triples (T) and quadruples (Q) as provided by a modest size MR CISD. The secondary triples are then accounted for via the standard perturbative-type (T)-correction by the RMR CCSD(T) method<sup>24–26</sup>. While in most cases the use of 2 to 4 dimensional model space is sufficient to account for nondynamic correlations, the breaking of a triple bond in N<sub>2</sub> required 56 dimensional reference space for a realistic description of the van der Waals region of geometries<sup>19</sup>. The computed vibrational frequencies agree reasonably well with those obtained experimentally and a qualitative agreement is also obtained with experiment-based analytic potentials of Le Roy et al.<sup>27</sup> (cf. Fig. 2 of ref.<sup>19</sup>).

In spite of the above mentioned successful generation of the N<sub>2</sub> PECs, there is no denying that serious computational problems arise when solving the electronic Schrödinger equation in quasidegenerate situations, often causing a serious departure from the correct shape of pertinent potential functions from their standard form (e.g., displaying a singular behavior in the van der Waals region of geometries), thus making them unsuitable for quantitative description of the fine features of ro-vibronic spectra involving energetically high-lying vibrational states.

One of the general, yet practical ways of overcoming the above problems consists in morphing approximate, but topologically correct, *ab initio* potentials by fitting to accurate experimental data (see, e.g., refs<sup>28,29</sup>). Such morphing procedure appears to be a suitable tool for a construction of molecular potentials, especially when it is combined with the reduced potential curve (RPC) method of Jenc<sup>30,31</sup> or its generalizations<sup>32,33</sup>. Recently<sup>34</sup>, for instance, this procedure has revealed the existence of the ‘elusive’ twelfth vibrational state of the beryllium dimer and its two rotational states. Furthermore, this procedure allowed for a correct assignment of the FTS spectra of highly excited, bound vibrational states of the lowest KRb triplet solely on the basis of experimental scattering lengths (cf. ref.<sup>35</sup>). The RPC based morphing procedure has already proved to be useful for probing of earlier generated SR-CCSD and RMR-CCSD potentials<sup>36</sup> that provide a computationally affordable molecular PECs over a reasonably wide range of vibrational distortions<sup>37</sup>. Importantly, performing a series of actual RPC based morphings for molecular nitrogen has revealed that approximate SR-CCSD and RMR-CCSD methods (see refs<sup>19,36</sup> and references therein) can provide a molecular potential that reproduces the available experimental data nearly as quantitatively as the highly accurate, yet computationally

demanding ( $r_{12}$ )-MR-ACPF *ab initio* potential of Gdanitz<sup>18</sup>. Relying on the agreement of morphings performed with potentials of a widely differing accuracy, it was surmised that at least the ( $r_{12}$ )-MR-ACPF variant should be capable of realistic predictions for the energy region that is significantly outside the region of observed energies. However, this conjecture does not appear to be strongly supported by results provided by the most recent studies<sup>27,38</sup>, as may be seen from Fig. 1, where we compare deviations of various empirical and theoretical<sup>18</sup> vibrational levels from those implied by the MLR<sub>4</sub>(6,8) potential of Le Roy et al.<sup>27</sup>. Thus, since a new set of highly accurate RMR-CCSD potentials<sup>19</sup> is now available for a ‘shape probing’, we have found it worthwhile to revisit the previous RPC determination<sup>37</sup> of the discussed potential with an emphasis on so-far unobserved high-lying vibrational states.

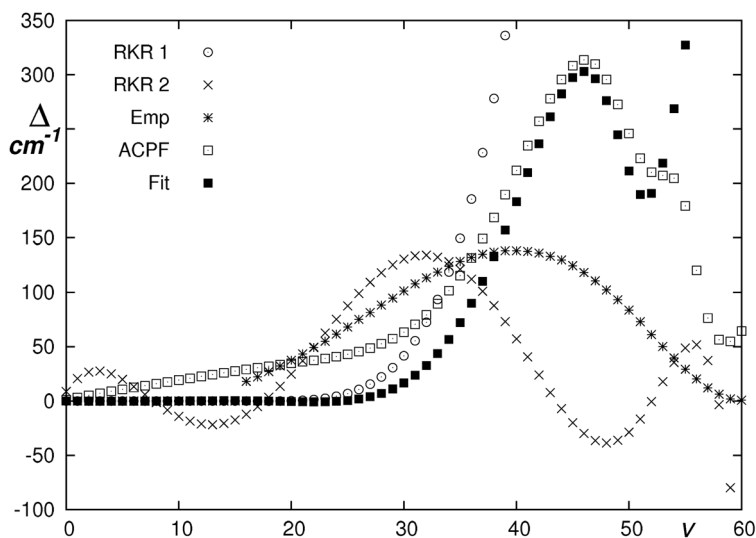


FIG. 1

Deviations ( $\Delta$ ) of the literature energies from the MLR<sub>4</sub>(6,8) values determined by LeRoy et al.<sup>27</sup> (EPAPS Document No. E-JCPSA6-125-014638);  $\nu$  is the vibrational quantum number. RKR 1, evaluated using the Dunham coefficients given in ref.<sup>27</sup>; RKR 2, evaluated using the Dunham coefficients given in ref.<sup>38</sup> (see Eq. (16)); Emp, empirically determined values (private communication from M. Lino da Silva); ACPF, evaluated using the ( $r_{12}$ )-MR-ACPF potential of Gdanitz<sup>18</sup>; Fit, values determined by morphing the ( $r_{12}$ )-MR-ACPF potential of Gdanitz by fitting to experimental data<sup>37</sup>

## METHODS

*The Reduced Potential*

The actual determination of the sought potential function is performed in two steps. First, a given (reference) *ab initio* potential energy function  $V^{ai}(R)$  is used to generate its reduced form  $u(\rho)$ , which is defined as follows

$$u(\rho) = V^{ai}(R)/D_e^{ai} \quad (1)$$

where  $D_e^{ai}$  is the depth of  $V^{ai}(R)$ , and the reduced variable  $\rho$  is related to  $R$  via the expression

$$\rho(R) = \frac{R - \rho_{ij} [1 - \exp(-R/\rho_{ij})]}{R_e^{ai} - \rho_{ij} [1 - \exp(-R/\rho_{ij})]} \quad (2)$$

Here  $R_e^{ai}$  designates the minimum distance for which  $V^{ai}(R)$  is available,  $\rho_{ij}$  satisfies the transcendental equation

$$\rho_{ij} = \frac{R_e^{ai} - \sqrt{\kappa D_e^{ai} / k_e}}{1 - \exp(-R_e^{ai} / \rho_{ij})} \quad (3)$$

where

$$k_e = (d^2 V^{ai} / dR^2)_{R=R_e^{ai}} \quad (4)$$

and, finally, the 'universal' reduced force constant  $\kappa$  is assumed to acquire its recommended value of 3.96 (see ref.<sup>31</sup>).

In the second step, the reducing procedure is reverted by expressing  $V(R)$  as the function of  $u(\rho)$ , namely

$$V(R) = D_e u(\rho), \quad (5)$$

with  $\rho \equiv \rho(R)$  defined by

$$\rho(R) = \frac{R - \rho_{ij} [1 - \alpha \exp(-\beta(1 + \gamma R)R / \rho_{ij})]}{R_e - \rho_{ij} [1 - \alpha \exp(-\beta(1 + \gamma R)R / \rho_{ij})]} \quad (6)$$

and involving a priori unknown parameters  $D_e$ ,  $R_e$ ,  $\rho_{ij}$ ,  $\alpha$ ,  $\beta$ , and  $\gamma$ , which are to be determined by fitting the available experimental data. In other words, the proposed reduced potential can serve as a six-parameter empirical po-

tential. Unlike the usually employed empirical potentials, the reduced potentials rely on a pointwise representation. Undoubtedly, on the one hand, this necessitates a numerical smoothing, thus making their use less convenient in comparison with analytically defined potentials. On the other hand, however, in cases when the shape of the actual potential significantly deviates from that of the standard empirical potentials, it is advantageous to use a few-parameter reduced potential rather than standard empirical potentials that usually require a much larger number of parameters (see, e.g., ref.<sup>39</sup>).

### *Ab initio Calculations*

The two *ab initio* potentials that are employed in our analysis differ significantly in the required computational effort. The ( $r_{12}$ )-MR-ACPF potential<sup>18</sup> was generated using a very large [11s9p6d4f2g1h] basis set while accounting at the same time for cusp singularities by considering terms that are linear in the interelectronic ( $r_{12}$ ) coordinates. In view of the large basis set employed the results were also corrected for the basis set superposition error (BSSE), which is quite significant at shorter internuclear separations. To warrant approximate size-extensivity, the MR CI method was combined with the MR-ACPF approach. Each iteration required ~8 h (with additional ~4 h for counterpoise correction) on Silicon Graphics Power Challenge R8000.

In contrast, the RMR-CCSD and RMR-CCSD(T) methods<sup>20,24–26</sup> are computationally much less demanding. Indeed, these methods employ a MR CISD wave function – based on as restricted a reference space as possible – that is used to generate a small subset of important (primary) three- and four-body cluster amplitudes. This requires a rather modest computational effort. Once this small subset of primary triples and quadruples is available, the evaluation of the required correcting terms (that are neglected in the standard SR CCSD approach) is again computationally affordable in view of the fact that only linear terms in these amplitudes are required and only a relatively small number of triples and quadruples is involved (for the handling of the  $T_1T_3$  terms as well as other details, see ref.<sup>20,21</sup>). When these correcting terms have been evaluated, once and for all, one has to solve only the standard SR CCSD equations. These calculations employed spherical Gaussian cc-pVXZ basis sets with X = D, T, and Q (the largest one amounting to an atomic orbital [5s4p3d2f1g] set) and a two- and three-parameter extrapolation to the “complete basis set” (cbs) limit<sup>19</sup>. The actual RMR calculations were based on a 56-dimensional refer-

ence space MR CISD, representing a minimal model space that can properly describe the dissociation of a triple bond (i.e., is size-consistent). The required computational time took couple of hours per point on a standard PC (for larger internuclear separations  $R$  a larger number of iterations was required). This enabled us to generate a dense grid in terms of the N–N interatomic distances  $R$  (cf. Table A-1 of the Supplementary material) facilitating a probing of the shape of the corresponding potentials in full detail and thus to assess the capabilities of the RMR-type approaches to generate computationally affordable potentials including significantly stretched geometries. The resulting potentials, and also their ‘cbs’ extrapolated and reduced forms, were smoothed using a combination of the exponential polynomials, cubic splines and orthogonal polynomials. In spite of a thorough search, no suitable empirical potential involving ‘only a few-parameters’ that would allow for a quantitative global fitting of the calculated *ab initio* data was found. On the one hand, this indicates a fairly nonstandard shape of the potential energy curve of N<sub>2</sub> in its ground electronic state and, on the other hand, gives a good reason for the use of the reduced potential curve (RPC) approach.

As a matter of fact, unlike their VDZ and VQZ analogues, some of the VTZ energies on the repulsive side of the potential do exhibit a sizable de-

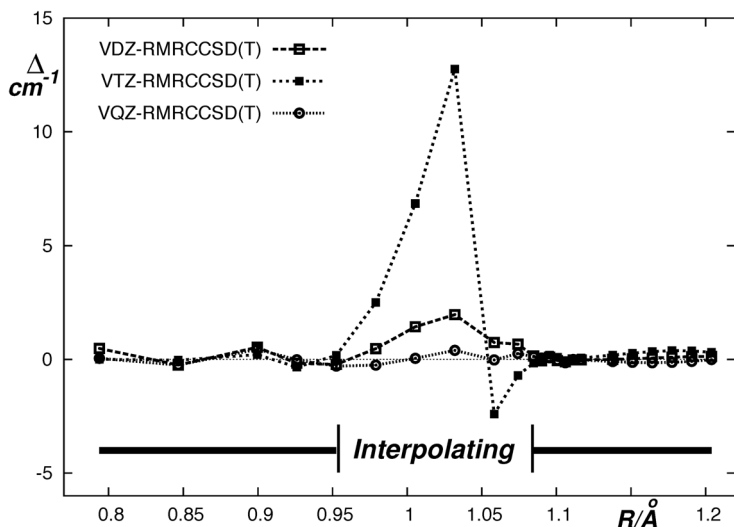


FIG. 2

Irregular behavior of the repulsive limb of the CCSD(T)/cc-pVTZ potential. T-X ≡ RMR-CCSD(T)/cc-pVXZ, where X = D, T and Q

parture from a smooth behavior predicted by global fittings based on the exponential polynomials. It should be stressed that the magnitudes of these deviations obtained for the CCSD energies are found to be much larger than for their CCSD(T) counterparts that are illustrated in Fig. 2. We have therefore decided to discard the RMR-CCSD/ccpVTZ data from our analysis.

## RESULTS AND DISCUSSION

We start by revisiting our earlier RPC determination of the probed potential. We thus first construct the  $(r_{12})$ -MR-ACPF based potential energy functions by fitting the same experimental data that were employed by Le Roy et al.<sup>27</sup> (see the Supplementary material of ref.<sup>27</sup>). As expected (cf. ref.<sup>37</sup>), such a RPC approach provides not only an essentially quantitative duplication of the fitted data while relying on only a three-parameter version of the proposed scheme (a consideration of additional parameters has a negligible effect; see Tables I and II). From the viewpoint of this study, it is even more important that the fitted variants of the probed potential energy function also predict highly excited vibrational states with a very high degree of coincidence (i.e., a bijection between these sets of states). In fact, as may be seen from the upper panel of Fig. 3, the dispersion (e.g., the standard or median quadratic deviation) of the  $(r_{12})$ -MR-ACPF energies as obtained with a fixed value of the dissociation energy  $D_e = 79\,845\text{ cm}^{-1}$  (referred to as the ‘interpolated’ energies) is smaller by about two orders of magnitude than is the dispersion pertaining to the potentials produced by Le Roy et al.<sup>27</sup>. As may have been expected (see the lower panel of Fig. 3), the dispersion of the ‘extrapolated’ energies (i.e., those obtained when allowing  $D_e$  to vary) is significantly larger than that of their ‘interpolated’ counterparts and, also not surprisingly, exhibits a small but non-negligible mass dependence associated with the mass-dependent biasing of the statistical weights of the fitted data.

This latter mass dependence, or at least some part of it, can be in principle attributed to the failure of the Born–Oppenheimer approximation (BOA). Unfortunately, until an adequate information on the shapes of the pertinent correcting terms (mass polarization, electronic angular momentum, first and second derivatives with respect to  $R$ , see, e.g., ref.<sup>40</sup>) is available, the simple RPC scheme, as adopted in this study, is not capable of a physically unambiguous rationalization of the discussed BOA failure. Nevertheless, the  $(r_{12})$ -MR-ACPF RPC scheme appears to represent a suitable and robust tool not only for predicting so-far unobserved vibrational states



(see Table A-2 of the Supplementary material), but also for probing the shapes of the RMR-CCSD potentials that we evaluate in this study.

The actual results concerning the probing of the RMR-CCSD potentials are illustrated in Figs 4 and 5. We can see that on the one hand the RMR-CCSD potentials do not provide reliable asymptotics (see the upper panel of Fig. 4) and thus cannot be used for predictions of higher-lying ro-

TABLE I  
The RPC parameters determined by morphing the ( $r_{12}$ )-MR-ACPF potential<sup>a</sup> with fixed  $D_e = 79\,845\text{ cm}^{-1}$

Parameter	Fit 1a	Fit 2a	Fit 3a	Fit 4a	Fit 5a	Fit 6a
$R_e, \text{ \AA}$	<b>1.097689</b>	<b>1.097689</b>	<b>1.097688</b>	<b>1.097688</b>	<b>1.097690</b>	<b>1.097689</b>
$\rho_{ij}, \text{ \AA}$	<b>0.746305</b>	<b>0.746227</b>	<b>0.746388</b>	<b>0.747174</b>	<b>0.745878</b>	<b>0.745695</b>
$D_e, \text{ cm}^{-1}$	79 845	79 845	79 845	79 845	79 845	79 845
$\alpha$	<b>1.000893</b>	<b>1.001733</b>	1.0	1.0	<b>1.002426</b>	1.0
$\beta$	<b>0.999296</b>	1.0	<b>0.998548</b>	1.0	1.0	<b>0.997139</b>
$\gamma, \text{ \AA}^{-1}$	0.0	0.0	0.0	<b>-0.002451</b>	<b>0.000972</b>	<b>0.002369</b>
S.D. <sup>b</sup>	0.039	0.040	0.040	0.041	0.040	0.040

<sup>a</sup> The potential taken from ref.<sup>18</sup>; the values of the fitted parameters are set in boldface.

<sup>b</sup> Standard deviation of the fit.

TABLE II  
The RPC parameters determined by morphing the ( $r_{12}$ )-MR-ACPF potential<sup>a</sup> with relaxed  $D_e$

Parameter	Fit 1a	Fit 2a	Fit 3a <sup>c</sup>	Fit 4a <sup>d</sup>	Fit 5a <sup>e</sup>
$R_e, \text{ \AA}$	<b>1.097702</b>	<b>1.097690</b>	<b>1.097690</b>	<b>1.097689</b>	<b>1.097689</b>
$\rho_{ij}, \text{ \AA}$	<b>0.744039</b>	<b>0.746501</b>	<b>0.746550</b>	<b>0.746307</b>	<b>0.746193</b>
$D_e, \text{ cm}^{-1}$	<b>80 048.27</b>	<b>79 819.70</b>	<b>79 815.06</b>	<b>79 838.40</b>	<b>79 848.04</b>
$\alpha$	1.0	<b>1.001940</b>	<b>1.001970</b>	<b>1.001812</b>	<b>1.001706</b>
$\beta$	1.0	1.0	1.0	1.0	1.0
$\gamma, \text{ \AA}^{-1}$	0.0	0.0	0.0	0.0	0.0
S.D. <sup>b</sup>	0.050	0.040	0.038	0.017	0.013

<sup>a</sup> The potential taken from ref.<sup>18</sup>; the values of the fitted parameters are set in boldface.

<sup>b</sup> Standard deviation of the fit. <sup>c</sup> Statistical weights of the <sup>14</sup>N<sup>15</sup>N and <sup>15</sup>N<sup>15</sup>N data were divided by 10. <sup>d</sup> Statistical weights of the <sup>14</sup>N<sup>14</sup>N and <sup>14</sup>N<sup>15</sup>N data were divided by 10. <sup>e</sup> Statistical weights of the <sup>14</sup>N<sup>14</sup>N and <sup>15</sup>N<sup>15</sup>N data were divided by 10.

vibrational states (and certainly not for an accurate estimate of the dissociation energy). Here we must recall that since the RMR CCSD method employs a SR exponential Ansatz and all the terms in RMR CCSD equations are

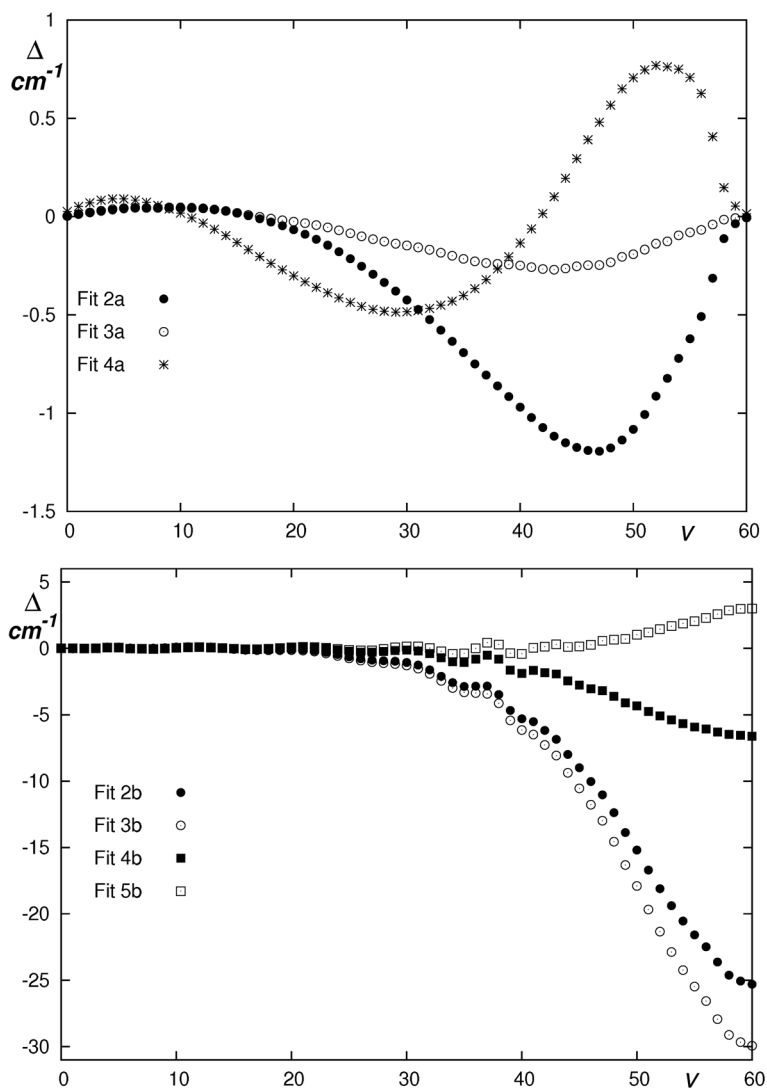


FIG. 3

Deviations ( $\Delta$ ) of the  $(r_{12})$ -MR-ACPF vibrational energies from their Fit 1a reference values (see Tables I and II);  $\nu$  is the vibrational quantum number

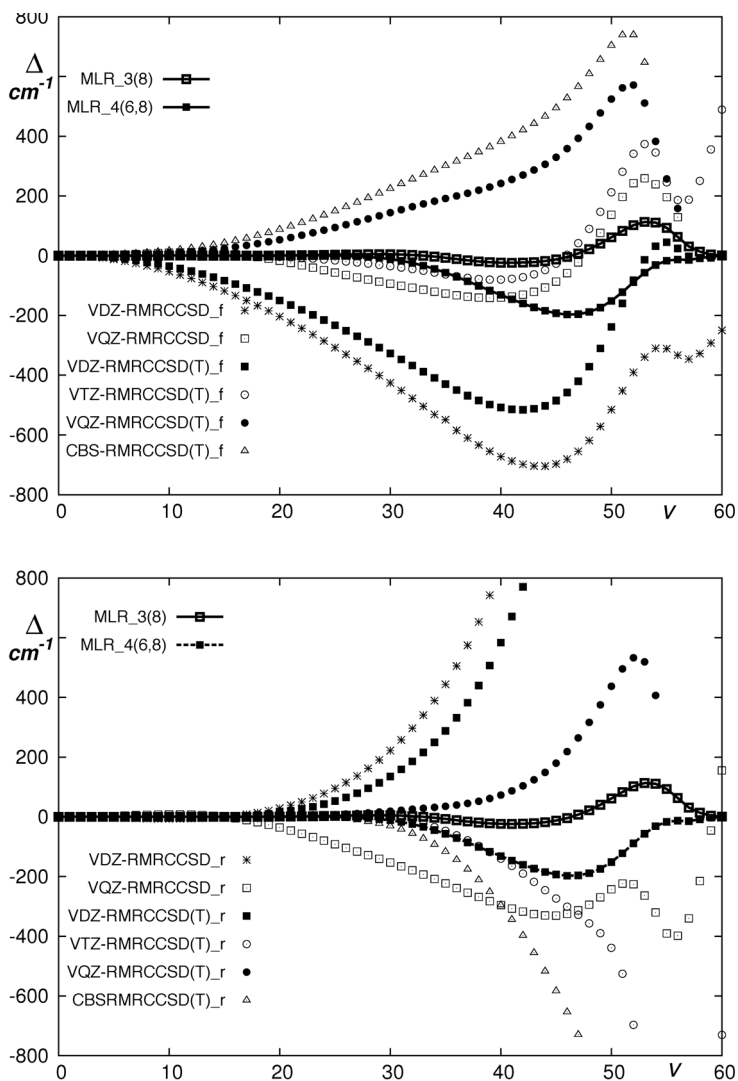


FIG. 4

Deviations ( $\Delta$ ) of the vibrational energies pertaining to the RMR-CCSD potentials from the Fit 1 (see Table I) reference values. VXZ implies cc-pVXZ, where X = D, T and Q; CBS pertains to the potential energy curve obtained by extrapolating to the complete basis set limit using the ccpVDZ and ccpVQZ potentials; subscripts 'f' and 'r' correspond to the results obtained with fixed and relaxed values of  $D_e$ , respectively (see Tables A and B of the Supplementary material);  $\nu$  is the vibrational quantum number

connected, it is size-extensive for all practical purposes (deviations amount to a fraction of a millihartree; see, e.g., ref.<sup>41</sup>). Thus, a slight violation of the exact size-extensivity arises due to a noniterative use of MRCI  $t_3$  and  $t_4$  amplitudes. When all  $t_3$  and  $t_4$  dependent terms are treated fully iteratively, as in the pIMR CCSD method<sup>42</sup>, the energies are exactly size-extensive (see Sec. IV of ref.<sup>41</sup>). Moreover, in the RMR-CCSD approach, the  $t_3$  and  $t_4$  amplitudes effectively represent all higher-excited amplitudes (using FCI 3- and 4-body amplitudes, the RMR-CCSD method recovers the FCI result) and the fact that in the van der Waals region of geometries the MR CI primary 3- and 4-body amplitudes may be expected to deviate more and more from the FCI ones, as well as a less adequate representation of the secondary triples the size of which will be augmented in this highly quasidegenerate region of geometries, are likely the source of the above mentioned behavior of PECs. Nonetheless, these potentials, especially those corrected for secondary triples via RMR-CCSD(T), allow for a rather accurate reproduction of the experimentally available data using only a modest number of the fitting parameters (see Fig. 5 and Tables A-3 and A-4 of the Supplementary material). This documents the ability of RMR approaches to provide a correct description of the 'lower' part of the molecular potential energy functions even for a highly challenging case of a triple-bond dissociation.

In closing this section, a few additional observations are in place. First, we wish to emphasize the ability of the RMR-CCSD and RMR-CCSD(T) approaches to achieve, at least qualitatively correct description of the PEC of nitrogen in the critical region of highly-stretched geometries. We recall that this is a particularly challenging task for CC approaches, since the standard SR-CCSD, and even more so the SR-CCSD(T) methods completely fail in this regard. Indeed, a minimal reference space that is required to achieve a triple bond breaking involves eight references<sup>43</sup>, yet a reasonably realistic RMR-type description required 56 references. However, not all currently available MR CC methods are capable of generating qualitatively correct PEC for  $N_2$ . In this regard, we point out to a very recent study<sup>44</sup>, which shows that both the state-selective Mukherjee MR CC and Brillouin–Wigner MR CC yield rather unsatisfactory results for the nitrogen molecule PEC even when a CAS(6,6) reference space (which is equivalent to our 56-dimensional reference space) is used.

We also recall that even careful empirical fits of all the available empirical data, relying on diverse analytical forms, produced significantly different PECs in this critical region of highly-stretched geometries<sup>27</sup>. It is thus encouraging that the RMR approaches yield PECs that nicely fit within the region of energies traced out by these empirical analytical potentials (cf.

Fig. 2 of ref.<sup>36</sup>). As far as we know, this is the only CC-type approach that yielded at least a qualitatively correct PEC bridging the bonding and dissociative regions of internuclear separations. This, however, could be

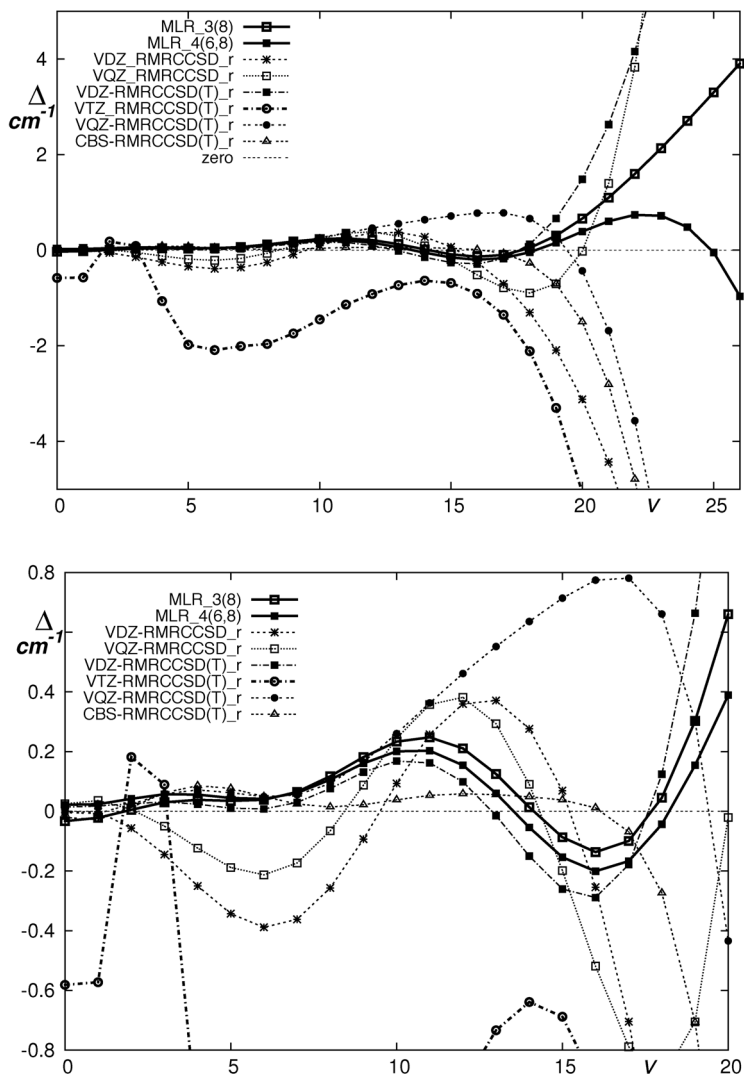


FIG. 5

Deviations of the vibrational energies pertaining to the 'relaxed' RMR-CCSD or RMR-CCSD(T) potentials (see Table B of the Supplementary material) from the Fit 1 (see Table I) reference values;  $\nu$  is the vibrational quantum number

only achieved by relying on a sizeable model space spanned by 56 references, a much larger model space in comparison with the two- or four-dimensional ones that are usually sufficient to describe single-bond dissociation process.

On the other hand, it is self-evident that once we consider the range of highly stretched geometries, we are far away from spectroscopic accuracy. Although the RMR-type approaches, at least when perturbatively corrected for secondary triples, achieve a reasonably good description of experimentally observed vibrational levels with  $\nu < 19$ , we find larger and larger deviations from the most reliable ( $r_{12}$ )-MR-ACPF theoretical values as the internuclear separations increase. The lower part of the PEC seems to be rather insensitive to the size of the basis set employed, even though the values extrapolated to the cbs limit certainly provide the best agreement. Interestingly enough, for  $\nu > 19$  the VDZ and VQZ results start abruptly to deviate from the ACPF reference values, the deviations having an opposite sign (cf. Fig. 4), implying only a qualitative nature of these potentials in the corresponding region of geometries. Clearly, a systematic use of larger basis sets, such as the even-tempered ones, a proper account of the core and core-valence correlations, as well as a careful extrapolation to the cbs limit (see, e.g., refs<sup>45,46</sup>, and references therein for such extrapolations in the CI context) would be desirable to further fine-tune the performance of the RMR-type methods in this challenging region. Nonetheless, the above presented results, particularly the ability of the RPC method to represent the RMR-type potentials with only a few parameters, are very encouraging. It would thus be certainly worthwhile to perform more extensive calculations and carry out their deeper analysis, to resolve the problem encountered when employing VTZ basis set and, eventually, to account for finer effects such as Born–Oppenheimer corrections, relativistic effects or long-range interactions.

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